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FEATURES OF CELLULOSE FIBER STRUCTURE SHOWN BY DIFFERENTIAL DYEING*

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Characteristic great differences in color have been observed when different cottons, especially cotton fibers of different degrees of development, have been dyed under specified conditions with a mixture of two particular contrasting direct dyes, a green and a red. Similar very different colors were obtained with different rayons when they were dyed together, with the same dye combination to aid in the understanding of the results obtained with cotton.

The pronounced differences in color are now explained in accordance with present-day views of the mechanism of direct dyeing and with some of the features of the submicroscopic structures of cellulose fibers. The color differences are due largely to the difference in size and shape between the green and red dyeing-units (presumably molecules, or anions) and to differences in accessibility, ie, in the "channels" for diffusion into and out of the cellulose. Movement tends to be rapid for the small red units and slow for the large green units.

Conversely, similar dyeings of unfamiliar cellulose fibers, such as treated cottons and new rayons, allow features of their submicroscopic structure to be recognized, so that conclusions drawn from the colors obtained in the dyeings will aid in characterizing the fibers.

INTRODUCTION

THE main purpose of this paper is to show the value of a wider use of dyeing in research on cellulose fibers. Dyeing with individual colors is frequently helpful for disclosing or confirming properties of fibers, but differential coloring with a dye mixture may tell much more. This discussion is concerned mainly with one dye combination which has proved to be especially useful with cotton *(8, 19)* but can give even more striking results with rayons. It has been used to a more limited extent with other fibrous cellulosic materials. Another purpose is to contribute to the explanation of the results of such dyeing to aid in their interpretation in terms of structure and properties of fibers of cellulose and various fibers derived from cellulose. Different contributing factors have been recognized and mentioned in several publications but explanations given so far have been incomplete or incorrect in some respects. Comments of others have been reviewed and the explanations are now extended from the authors' own observations. The original observations were that a mixture of two particular substantive dyes, a green and a red, colored certain fibers green and others red, in great contrast, in each of hundreds of samples of cotton from many sources, when suitably dyed and hot washed. Since then, many special dyeings on rayon as well as cotton have helped to explain why tufts of natural raw cotton may dye so differently in the same dyebath; and why different rayons also may dye in the same bath to various colors, from green to red.

Since the differences between the colors of the dyed cellulose fibers must depend very greatly upon submicroscopic structural differences, dyeings of cellulose fibers with known characteristics may help to characterize, in a qualitative way, fibers similarly dyed whose submicroscopic structure is not known. However, it must be recognized that differences between structures indicated by dyeing apply to the fibers when swollen in dyebaths. They may not necessarily indicate the properties of the fibers in their ordinary dry state but are no doubt closely related to them.

BACKGROUND

The first reference known to the authors related to the present type of work, is a description of a test in which a direct blue, a yellow, and a red were employed at the Shirley Institute in England in dyeing a sensitive gray shade to emphasize defects in mercerized cotton yarn *(5)*. This combination of dyes could not be stripped completely with hydrosulfite, which happened to be desired, but a nearly equivalent dyeing combination which could be stripped was found in a green, Chlorantine Fast Green BLL[3] (Ciba) *(1)*, used in place of the blue and yellow, and the original red, now employed under the name Diphenyl Fast Red 5BL Supra I (Geigy) *(1)*.

The green and red dye combination was found years later at the Southern Regional Research Laboratory to distinguish so-called immature cotton fibers from mature fibers *(8)*. Cotton is a seed hair, but similar responses with ramie, a bast fiber, and with rayons show that the differential dyeing behavior does not depend upon anything peculiar to cotton alone but upon more general properties shared by various cellulose fibers.

Other dye combinations, in addition to those used for studying skin and core relationships, have been employed with rayons. Harrison *(15*, discussion) mentioned work with acid and direct dyes used together to dye selectively ordinary and highly stretched viscose rayons, and he was of the opinion that "varying accessibility accounts for most of the

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[3] The use of trade names and those of manufacturers of dyes or fibers is for information only, and does not imply endorsement by the Department of Agriculture over similar products not mentioned.

curious results obtained." Combinations of blue direct and red acid dyes have been used for distinguishing between viscose and cuprammonium rayons, their differential staining being explained by Preston *(14)* as due to different rates of dyeing and different affinities in conjunction with the different degrees of openness of structure of the rayons of the two types.

Dye mixtures used as stains for the identification of various kinds of fibers represent a somewhat different type of application, although they may have effects which appear similar to some of those to be described. A dye combination used by Simons *(18)* in a stain test for beaten pulp has been found also to have differential coloring properties when dyed at the boil on cellulose fibers, and is taken up below.

METHOD OF DYEING

The procedure *(8, 19)* is that of direct dyeing with a fairly high percentage of color (4%) and a relatively low percentage of salt (5%), on the weight of the fiber being dyed. The proportions are 2.8% of the green and 1.2% of the red, in a total bath of 40 times the weight of the fiber. The salt is added, after dyeing without it for 15 minutes, in two equal portions 15 minutes apart and dyeing is continued to a total of 45 minutes. Dyeing is followed by cold rinsing, then by a desorption step, a hot wash or "stripping" not employed in ordinary direct dyeing. This comprises dipping the dyed materials in boiling water for 30 seconds, usually while still wet. Such stripping can, however, be done after drying with little apparent difference in results. Differential dyeing can be understood to mean dyeing plus hot water stripping unless it is clear that dyeing alone is meant.

The green and red dyes used are roughly complementary colors which tend to dye gray. Fibers colored predominently with either dye are usually dulled or grayed by a smaller proportion of the other, but occasionally the nearly individual or "self" shade is obtained. The significant differences in color are easily observed without the use of optical instruments, so the present discussion is entirely qualitative as based on visual observations.

A few of the characteristics of the particular dyes used are given here to facilitate the descriptions and suggested explanations of results. Their behavior in dyeing depends upon their constitutions, and no doubt greatly upon the great difference in their molecular weights which are about 1350 and 675 for the green and red, respectively *(4, 16)*. If dyeing at the boil takes place mainly by individual dye molecules (*12; 20,* p 186), the effective dyeing unit of the green is appreciably larger than that of the red and there is, apparently, also a shape factor which adds to the difference in dyeing behavior of the two dyes. The red has essentially a straight chain molecule, "now generally recognized as an essential attribute of a substantive direct dye" (*20,* p 173). Whether or not this shape favors diffusion into cellulose fibers, it is regarded as favoring fixation along cellulose chains. The green has a branch which which may have much more effect on dyeing than an equivalent extra length of chain. For convenience the green will be referred to as the large or larger dye molecule without the shape qualification.

Observed effects of differential dyeing have been attributed to rates of dyeing, apparently as though a rate of dyeing were a definite dye property. This was probably not intended because a rate is not a property of a dye although a given dye might adsorb on most cellulose fibers more rapidly or more slowly than some other dye. Two dyes as different in size and shape as the green and red would be expected to dye at different rates on almost any cellulose fiber. Such differences, and differences in rates of dyeing of a given dye from fiber to fiber depend very greatly upon accessibility. Accessibility is used here as an overall term for effectiveness of contact of dye molecules with adsorption (*20,* p 8) sites of fibers for direct dyes in a dyebath. When cellulose or chemically modified cellulose fibers have such sites, accessibility to them depends upon the amount of fiber surface in contact with the dyebath, which increases greatly with decrease in diameter of fiber, or in denier of filament; upon channels for diffusion and distances through which dyes must diffuse to penetrate the fiber; and upon the size and shape of the molecule of the dye in relation to the spaces into which it seeks to penetrate. As dyes and fibers interact, observations and known facts about them help to extend our knowledge of both.

Another factor involving properties of dyes should probably be taken into account, if it could be. From incidental observations it has seemed that in some dyeings there is also interaction between dyes, such as displacement of one dye from dyeing sites by another; but there is insufficient knowledge in this field for its consideration here.

RESULTS OBTAINED WITH VARIOUS FIBERS

The relations between colors obtained in dyeing and fiber properties will be approached through descriptions and explanations of the dyeings of fibers whose properties may be regarded as known. While much of the following material has been published, it is reviewed here as necessary for the discussion of new applications of the differential dyeing technique, and of suggested explanations of observed differences of coloration of different fibers.

DYEING OF COTTON——The green and red fibers of differentially dyed cotton correspond very closely with fibers commonly designated as immature and mature, respectively, These terms, immature and mature, are widely employed to designate cotton fibers which are thin- or thick-walled relatively to total fiber width, according to a particular definition. Since the terms are relative, well-developed walls of fine cottons, which would be rated thick, are sometimes much thinner than comparable thick walls of coarse cottons. The red-dyeing fibers of both are colored to pronounced reds and although the finer red-dyeing fibers have been observed to take up slightly more green with the red than coarse fibers, they are dyed essentially alike. This means that fibers which would be considered mature, from all cottons, must be of substantially the same submicroscopic structure, as far as dyeing is concerned.

That structure may be a main determining factor for the color is shown most convincingly by the dyeing of dried and undried locks of cotton taken from the same boll, picked just before it would have opened naturally on the plant *(9)*, and is based on the fact that the fibers from one lock to another of a given normal boll are, on the whole, alike. When one such lock was dried and another kept undried, and both were then dyed in the same bath with the green-red formula, they came out very different. The fibers in the first were red after dyeing and hot water stripping, except for definitely immature fibers which were colored green in accordance with their usual behavior. The fibers in the second (undried) lock were dyed with both red and green and approached black, but came out

green from the loss of most of the red on the hot water stripping.

The explanation of these effects follows from the well known fact that cellulose is deposited in the moist cotton fiber in the boll in a far more voluminous form than that of normally dried fibers. When it had never been dried it was of very open structure which readily admitted the green. In contrast, cotton dried for the first time undergoes a drastic change in volume as the fibers collapse. The dried fibers had become so compact in structure as no longer to admit the green, although they still admitted the red which dyed the fiber throughout.

Although we have regarded cotton as a known fiber, differential dyeing has brought out a difference between cotton fibers which has not been recognized heretofore. When seen in cross section under the microscope, following a differential dyeing, the thicker, rounder fibers are red, and thin flat fibers are green but there are frequently cross sections of intermediate size, some red and some green, which are so nearly alike in size and shape that size alone could not possibly have determined the color. It can only be concluded that these green fibers and the green-dyeing fibers which are more obviously thin-walled are different in structure from red-dyeing fibers.

The sharp separation of the green and red fibers, and the fact that the dyeing follows in a general way maturity as commonly recognized, show that there is some more natural basis of distinction between fibers than an arbitrary one based on wall thickness. Since it probably has a more fundamental basis, this distinction may prove to be more significant for the utilization of cotton than determinations of maturity.

According, then, to considerations presented above, the green-dyeing of certain fibers is attributable to greater openness of structure, at least when swollen in a dyebath. It can be presumed that some such difference exists also in the dry fibers and it appears to offer a fundamental basis for characterizing cotton fibers. Up to the present, this distinction has not been shown in any other way than by differential dyeing.

Armfield and Boulton *(2)* suggest substantially the same explanation (below) for the green and red dyeing of thin- and thick-walled cotton fibers as for rayons of different denier. However, similarity of structure is necessary within a group of fibers if the rules are to apply, and their explanation for cotton is not complete because it did not allow for the difference in structure discussed above.

DYEING OF RAMIE——An early indication that the differential dyeing effect is not peculiar to cotton alone was afforded by dyeings of ramie *(7)*. A strand of this bast fiber "21 days old" dyed all green; and a much longer strand "42 days old" dyed mainly red, but green at one end. The green portion was obviously the younger, or top, growing end of the strand. The microscope confirmed this view; the fibers which dyed green were much like thin-walled cotton fibers in cross section, while those that dyed red looked like thick-walled cotton fibers. From evidence contributed by cotton, and cuprammonium rayon (below), it can safely be concluded that the fibers of the green-dyeing portions of the ramie strand were more open in structure, probably when dry as well as when wet.

DYEING OF RAYONS——Rayons were dyed particularly for possible help in explaining the differential effects obtained with cotton. First were three samples of viscose rayon supposed to differ only in filament denier. Their colors were different after dyeing, but showed a much greater difference after hot water stripping, with a pronounced trend from green to red, from 1.66 to 6 filament denier, fine to coarse.

Similar dyeings made by Armfield and Boulton *(2)*, were even more striking because of a much wider range of filament deniers. They explained the progressive differences in the colors produced on viscose staple ("Fibro") of different deniers as due to two principal factors: First, the very different diffusing rates of the two dyes, as indicated by "times-of-half-dyeing." Boulton's data *(3)* show the red to be adsorbed more than 60 times as rapidly as the green on a particular rayon. It would be desorbed also at a greater rate. Second, the difference in dyeing behavior of coarse and fine filaments. The fine filaments dye more rapidly because of more surface in contact with the dyebath; also, for optical reasons, more dye is required to yield a given depth of shade, as judged visually. These influences work together to yield the results described and they are probably adequate to explain the differential effects when the only major variable is filament denier. If other conditions are comparable, viscose rayons can be placed in the order of filament denier by the green-red differential dyeing. The greener colors of fine filament viscose rayons have not approached as near to the pure green color as other green-dyed fibers under discussion. The greenish color of the former has been due to fineness and greater superficial surface with corresponding greater absorption and retention of green, and to easy loss of red rather than to greater openness of structure. Considerable red has remained in the viscose rayons and such differences in color as it causes are easily recognized.

Influences which cause variation in color according to filament denier cannot be expected necessarily to be determinative if there are also pronounced differences in structure between filaments being compared. Armfield and Boulton obtained green with cuprammonium rayon of 1.33 filament denier and "red" with viscose rayon of 5.6 denier. They explain this result as a consequence of the very great difference in dye absorption rates of the two fibers, of the difference in filament denier, and of the same general considerations as applied to the viscose series. This is not entirely correct in that the explanation is not the same as that for viscose rayons of different filament denier.

In the present work, five Bemberg (cuprammonium) rayons including both continuous filament and staple types, with filament deniers of 1.33 to 7.5, came out alike, of nearly the pure green color after differential dyeing and stripping, except for differences in depth of shade. There was no evidence of a differential effect within the series, as there would have been in a similar series of viscose rayons; and all were entirely different in color from the reddish gray of textile and tire cord viscose rayons dyed along with them, whose deniers fell between those of two of the green-dyeing Bemberg rayons. The different kinds of rayon would have dyed with approximately the same difference in color even if they had been equal in denier. Hence, size of filament had no significant effect in the determination of the great difference in color. This was shown even more convincingly by a dyeing of several rayons together, whose filament deniers were nearly equal but some of whose resulting colors were most extreme. Cuprammonium rayon of a filament denier of 2.08 dyed nearly pure green; Fiber G (see below) of 2 denier dyed nearly the pure red; while Cordura tire cord rayon of 2.29 and a textile viscose rayon of 2.5 denier dyed to an intermediate reddish gray color.

Since cuprammonium rayon dye-

ings take on much red but easily part with it almost completely, leaving the equivalent of at least a 1% to 2% green shade, higher affinity of the green is suggested in addition to greater accessibility to the fiber. The green appears to have a higher affinity for the fibers than the red. While it is immaterial for the moment whether the retention of the green is due to high affinity, or to a very low desorption rate, both may contribute. Evidence of higher affinity of the green is afforded by much greater apparent fastness to boiling water in connection with certain differential dyeings on cotton (see below).

In spite of other possibilities, the distinctive green-dyeing of Bemberg rayon is probably due mainly to some feature of its submicroscopic structure. Much has been written on the differences in structure between the filaments of cuprammonium and other rayons. The main point of present interest is that cuprammonium is well known for taking up dyes much more readily, is generally considered to be of more open or porous structure, and may even have open channels when dry. Differences between cuprammonium and viscose rayons have been reviewed by Vickerstaff (*20*, pages 269 and 278). When swollen in a dyebath the former is considered open at least in the sense that the large green dye molecules can enter between micelles and diffuse among cellulose chains that may be in the amorphous regions, as compared with certain other rayons and mature cotton fibers from which they are excluded under the same dyeing conditions. Since the Bemberg rayon fibers are dyed throughout, as verified from cross sections under the microscope, their dyeing green is taken as one of the indications that any fiber which might dye green in this same way would be of open structure, at least when swollen in a dyebath.

In contrast is Fortisan which dyed almost the pure red in the same dyeing in which the five Bemberg rayons dyed green and other rayons to intermediate colors. Samples of two Fortisans dyed to red shades of only moderate depth, but were seen under the microscope to be dyed throughout their cross sections. They lost a hardly preceptible amount of the color in the usual stripping with hot water, in contrast to thick-walled cotton fibers which would have dyed much darker and come down to half that depth. The rather moderate degree of uniform penetration by the small red molecules and their strong retention must be explained by a closely packed structure which is, in turn, partly explained by Fortisan's consisting of highly oriented cellulose chains because it is highly stretched during its production *(21)*.

The general conclusion seems justified from experience with both cotton and Fortisan that peristent very red dyeing means that the fiber structure is relatively nonporous throughout, at least in the sense of accessibility to dyes.

Differential dyeing can sometimes show visually a regular progression in change of color and structure, with a change in one variable in the treatment of a fiber, and thus serve to verify a change or a result. For example, a set of viscose rayons representing different degrees of stretch from 1-50% retained colors from greenish gray to much redder. As the stretch increased there was less dyeing with the green in accordance with Preston and Kapadia's general statement that the effect of orientation on dyeing is one of differing accessibility *(15)*.

NEW APPLICATIONS OF DIFFERENTIAL DYEING

Fibers, some of whose properties were not known, were dyed to obtain more evidence as to their nature. The usual green-red differential dyeing formula has proved useful, and can apparently serve as a basis for such dyeings of any cellulose fiber, including physically and sometimes chemically modified fibers, especially cotton. Dyeings are best made in comparison with known similar fibers preferably present in the dyebath at the same time; and the results obtained can naturally be understood and interpreted better if the history of the fibers is known. In a few examples, dyeings showed or confirmed some particular characteristics of fibers.

DYEINGS OF SPECIAL RAYONS ———Viscose rayons designated as having thick, thin, very thin and no skin, dyed from a red gray toward red, but the last represented a great change to almost the pure shade of the red. Upon stripping, the colors shifted toward gray from loss of red except that the no-skin rayon remained red and lost no appreciable depth by stripping. This no-skin rayon dyed just like Fortisan which indicates that this sample had an unusually nonporous structure since it was penetrable by the small red dye molecules but was almost unaffected by the green.

A sample of Fiber G (du Pont) dyed like the Fortisans except a little darker. The color showed that the fiber had a densely packed structure, probably brought about by a high degree of stretch; but did not indicate whether it was made like Fortisan or from viscose *(10)*. Either might seem possible from dyeings of other rayons already described.

A pronounced effect of change of structure was shown by means of Fortisan, which is said not to dye readily with direct colors but to have its "affinity" increased by pretreatment with caustic soda. Any appreciable treatment of this sort would naturally disrupt the fiber structure. As an extreme effect, "mercerized" Fortisan fabric came out green if dyed while still wet from washing out the caustic, and the effect was more pronounced at 9% than at several higher concentrations. When dyed together, untreated Fortisan was colored the usual red; the Fortisan that was allowed to shrink freely in the alkali, then washed, neutralized, washed and dried, dyed a rather dark grayed red, and stripped to a much lighter nearly neutral gray. When dyed before drying it came out a dark nearly neutral gray and stripped with loss of practically all the red to nearly the pure green. This result was due to change in fiber structure in the direction of greater accessibility to the green or greater porosity.

A rayon identified only as "BX" was dyed along with other rayons. The general description *(6)* probably applies, that it was stretch spun into a strong sulfuric acid bath from especially prepared viscose of a high degree of polymerization. Its filament denier was 0.5 or less. It dyed a neutral gray in contrast to tire cord and textile rayons, which dyed about alike and much redder. Since it took up relatively more green and retained less red, it gives the effect of a somewhat more open structure. If the coloring was largely a denier effect it should have been much greener yet. BX fiber is described as having numerous microcavities or interfibrillar spaces which facilitate dyeing. If this is so and the spaces admit the green as well as the red, and the latter then strips out as usual, the minute more open regions may hold the green preferentially, while more tightly packed parts of the structure may retain red, together to yield the overall gray color.

The latter resembled the color obtained in the differential dyeing of Durafil (Lilienfeld rayon), not available for checking, as recalled from dyeings by Armfield and Boulton, which were seen. The explanation might be similar but there is no other evidence for it than the dyeings.

Thus the differential dyeing technique shows in a new way that there is some fundamental structural difference between different highly stretched and highly oriented rayons, even though its evidence is not yet fully explained.

DYEING OF MODIFIED COTTONS———Dyeing with combinations such as the green-red is believed to have special value in helping to characterize cottons modified by chemical processes such as decrystallization *(17)* by ethylamine. Ordinary Cotton which originally dyed red, or kierboiled or bleached cotton which dyed gray, came out green when dyed at a suitable stage after decrystallizing. This was taken as evidence that the cotton had been made more open in structure, and that the proportion of amorphous cellulose had probably increased. When, however, the amine-treated cloth was freed from reagents in different ways and dried, it dyed very differently. The original bleached cloth dyed to the usual type of gray color, not as red as unbleached cotton. Treated cloth freed from ethylamine by solvent exchange with chloroform dyed almost the same, but a little darker. In great contrast, however, the cloth freed from ethylamine by distillation by heating at moderate temperature on a water bath dyed a pronounced, although not pure, red.

The dyeing thus indicates that the cloth which had the ethylamine removed by chloroform had apparently reverted nearly to its original state as bleached. It may have had a little more amorphous cellulose as indicated by its depth of shade, but apparently was little more open in structure at this stage than the original bleached cloth, since it obviously admitted very little more of the green dye. The cotton freed from ethylamine by distillation was still less accessible to the green. Its red color indicates that the cotton fibers then had a compact structure—that they may have "collapsed" from the distended, decrystallized, green-dyeing form in somewhat the same way as cotton fibers collapse when they dry in the boll, and change from green-dyeing to red-dyeing *(9)*. Whatever the state of the cellulose—whether or not the crystalline fraction is mainly Cellulose III—the dyeing indicates that it is of more compact submicroscopic structure.

Dyeings were much the same on similarly treated yarns but deeper shades indicated that the yarns had been modified more than the cloth. Thus the green-red differential dyeings of decrystallized cottons showed that a step by step dyeing study during such treatments might give definite indications regarding changes in the cotton cellulose.

SUPPLEMENTARY NOTES ON DYEING

Several factors important for the dyeing of direct colors seem to be of less importance than might be expected for the determination of differential effects, but can hardly be omitted from consideration.

The absorption of direct dyes has been attributed mainly to the amorphous portions, including micellar surfaces of the cellulose fibers, and the amounts of dye taken up have sometimes been considered to be roughly proportional to the amounts of amorphous cellulose present. The amounts alone cannot, however, be the determining factor between fibers of a given class because if it were, the two dyes would tend to go on together and come off together, and there might be differences in depth between fibers but not pronounced differences in hue. This leaves differences in fiber structures and in fiber sizes, which largely control accessibility to the amorphous cellulose, as apparently more important factors than the amounts present.

It is important also to consider whether affinity of dye for cellulose is a determining factor. Affinity is a term frequently used loosely for the attraction of dye for fiber as taken up and held under any particular conditions of dyeing, as when the green is retained predominantly by one type of cotton fiber and the red by another. True affinity is a concept limited to the "standard change of free energy" involved in the attachment of a molecule of dye to a cellulose substrate, and the affinity of a given dye should be the same for all celluloses. Marshall and Peters *(11)* determined for a number of dyes that the affinities of a given dye are approximately the same for four quite different cellulose fibers, namely, cuprammonium and viscose rayons, and mercerized and unmercerized cottons. They concluded that differences in dyeing behavior must be accounted for by purely physical differences between fibers rather than by differences in the affinity of the celluloses of different fibers for a given dye.

On the other hand, different dyes may have different affinities for the same cellulose, but sufficient data to aid in differential dyeing explanations are not available. In their absence, observations on fastness to hot water have been made. That there is a great difference in the relative fastness of the two dyes was shown qualitatively in two ways which are of special interest. In the first, the green and red were dyed on mature and on immature cottons, each singly in the same amount and by the same method as employed in differential dyeing; shades of medium depth resulted. Upon hot water stripping, the red-dyed cottons appeared to have lost half or more of their color, but the green-dyed cottons almost none. In the second case, a mature cotton, an immature, and an intermediate cotton were dyed differentially and stripped; and came out as usual, dull red, nearly green, and intermediate in shade, respectively. Additional stripping by two 15-minute boils in distilled water took out practically all the red and left the three samples colored to nearly equal tints with green. Thus, most of the green survived 30 to 60 times as long a period of boiling as most of the red. The green was not merely much faster but, for practical purposes, did not come off of the cotton.

The red penetrated all through the fibers in both of the types of dyeing just described, but cross sections showed under the microscope that the green penetrated only the thin-walled fibers and not visibly into the thick-walled fibers. The red diffused out readily but the green was very fast, and can hardly be said to have diffused since it appeared to be on the outsides only of all but the thin-walled fibers. The rates of removal of the red and green are of determining significance for differential dyeing and the difference between them is so great under the usual conditions that it seems immaterial here, as with cuprammonium rayon, whether the result depends upon differences in affinity or in rates of desorption.

The question whether noncellulose constituents determine the colors in the differential dyeing of cotton has been raised because there are considerable differences in the amounts present in mature and immature fibers. They would hardly be expected to have much effect in view of the fact that rayons with no such constituents show similar differences in dyeing. As more definite evidence, mature and immature cottons continue to show pronounced contrasts after they have been purified, even though boiling and bleaching, for example, make all cottons dye grayer or greener, evidently owing to some increase in accessibility or of surface adsorption.

Recent determinations indicate that a pronounced difference between the

amounts of swelling of mature and immature fibers in water may be significant. A centrifuge technique employed for the determination of the swelling of cotton (data not yet published) gave 50% swelling for a cotton of 85% maturity, and 70% for one of 30% maturity (very immature). The higher degree of swelling is no doubt associated with the more open structure of the immature cotton fibers in dyebaths and their greater receptivity for the green dye.

The far greater swelling due to mercerization might be expected to have an equalizing effect on all cotton fibers, and it may to some degree. Although the visible result from the differential dyeing of mature and immature cottons mercerized under various conditions is a considerable change in the colors of both, pronounced contrasts are maintained.

The concept frequently stated or implied in the literature that direct dyes diffuse into cellulose through open channels is apparently greatly oversimplified. It is a case of diffusion, hindered in several ways, between micellar regions through swollen amorphous cellulose. In the published discussion of a paper by Preston and Kapadia *(15)*, Preston and Entwistle are in general agreement that the spaces or channels in the amorphous cellulose are not entirely open, but that segments of cellulose chains may move about in them under thermal agitation. Entwistle thinks of the dye molecules as thus diffusing through a viscous solution of cellulose, while Preston suggests similarity to a bead curtain swaying in the wind, rather than to a fixed trellis barrier, with the dye molecules trying to find their way through. Differential dyeing results indicate that there must be differences in the degree of openness of these systems in different fibers; and the more open, the greener they dye.

OTHER DIFFERENTIALLY DYEING COLORS

Since there are innumerable possible combinations of direct dyes, and variations in the methods of dyeing them, there may be other, and perhaps better combinations for some purposes than the green and red. Many combinations of commercial dyes have been tried, selected largely on the basis of recognized differences in properties or in molecular weights, and particularly for complementary colors for good contrasts. Pronounced differences in the colors of immature and mature cotton fibers and of some rayons were found, but nothing that would be obviously better for the immediate purpose, which was the study of cotton.

One special combination seems, however, to deserve more attention because it indicates again that a shape factor may be not only important, but possibly determinative under some conditions for differential dyeing. This was the combination mentioned above, used as a stain by Simons *(18)* for differential coloring of fibers to show changes during the beating cycle in paper manufacture. His preferred dye combination is Pontamine Fast Orange 6RN (Du Pont) (*CI* 621) and Pontamine Sky Blue 6BX Greenish (Du Pont) (*CI* 518).

That such an orange might be useful as a component of differential dyeing formulas was suggested by the use of a similar dye, Erie Fast Orange CG (National) (*CI* 621) in old Bureau of Standards and ASTM methods for distinguishing cuprammonium from viscose rayons. The same type of dyestuff was reported later *(13)* under the name Calcomine Orange 5RE (Calco) (*CI* 621) as dyeing Bemberg rayon very differently from viscose. Experimental use indicated that the dyes sold under these three names are not all identical, although closely related according to *Colour Index (16)* and *Year Book (1)*.

The Orange CG and a sky blue (*CI* 518) had been tried for differential dyeing and found to be especially effective for identifying extremely thin-walled nep-forming cotton fibers. When this combination was dyed in the same general manner as in the green-red technique on fibers which have given greater contrasts than cotton, the blue of molecular weight about 990 colored Fortisan selectively and behaved in general more like the red (mw 675) than like the green. On the other hand, the orange (mw 820) acted more like the green (mw 1350) and went strongly on Bemberg rayon. The molecular weight of the orange is so far below that of the green that it alone cannot possibly account for the similarity. In the relatively few dyeings made, the orange penetrated some fibers with difficulty and did not diffuse out readily from those that it did penetrate. Its behavior seems distinctive, apparently because of its constitution. The dye molecule is shown as a closed ring *(16)* rather than elongated in shape, as is common for direct dyes. The apparently lower rate of diffusion might be due to molecular shape or to aggregation into larger dyeing-units[4].

The only other dye of similar ring form found in the *Colour Index* is represented by the closely related group which includes Erie Yellow F (National) (*CI* 620) which, in a few limited trials, behaved much like the orange[4].

These observations indicate again that the molecular weight feature of the explanation is oversimplified and inadequate alone; but that the essential points are difference in accessibility of dyes, by reason of size or shape, to fibers whose extremes are represented by those of highly compact and of relatively very porous structures at the submicroscopic level.

SUMMARY

Different cellulose fibers dyed together with a mixture of a particular green and a particular red direct dye, may come out very different in color; and the colors may yield new qualitative information about them if the properties of the fibers are not fully known. The results depend upon both, differences between the two dyes and upon differences between the fibers. The dyes differ greatly in molecular weight or size, and significantly in shape. The fibers that dye very differently do so because they differ in accessibility to the dyes.

The initial observation was that immature cotton fibers retain green selectively, and mature fibers red, when suitably dyed with this combination and dipped into boiling water for 30 seconds. The key was given by dyeing cotton fibers which were not dried between their removal moist from the boll and entry into the dyebath of the mixed dyes, and cuprammonium rayon, both of which dyed to full shades of green; also by dyeing Fortisan which, if dyed under the same conditions will come out nearly the pure red. The green-dyeing fibers are of very open or porous structure while swollen in the dyebath; and the red-dyeing Fortisan is the opposite, very nonporous.

These dyed fibers, with the known difference between the dyes, point to a fundamental difference between immature and mature cotton fibers, in porosity while in the dyebath, and probably also in compactness of structure in their ordinary dry state. This difference has not been shown by other means.

[4] H E Woodward (Lubs, H A, Editor, "The Chemistry of Synthetic Dyes and Pigments," 1955, page 120) notes that the ring structures shown for the dyes in the *Colour Index* under No.'s 620 and 621 are not accepted by I G Farbenindustrie chemists, but that the suggested alternative structures are not adequately supported by published experimental data. The new structures are given by A H Knight (*J Soc Dyers Col* 66, 47, 1950) as each consisting of two of the appropriate ring units opened and joined together as long chain molecules. If the linear form is correct, the possible contribution of the ring shape to the slowing of dye diffusion may be regarded as replaced by the effect of the doubling of the molecular weight, to more than 1600. It may be interesting to note also that in *Das Papier* 9, 507 (1955) Jayme and Harders-Steinhauser discuss the use of the Simons blue-orange dye combination, but recommend the use of a combination of their own, the same blue with a yellow, in work on pulp for paper. Their yellow is Benzo Fast Yellow A Ex Conc, another brand of the same dye, *CI* 520.

By dyeing fibers whose characteristics may not be known along with reference fibers of known dyeing and structural features, more can be learned about those of unknown properties. Other examples are given which include rayons and chemically modified cotton fibers to show that the technique is very promising for studies of new fibers and of modification processes, and of effects of changes in some of their important variables.

The value of the wider use of dyeing, which can be very readily performed, has been shown. Former explanations of such differential dyeing have been corrected and extended in accordance with original observations.

ACKNOWLEDGMENT

It is impossible to acknowledge specifically the help, direct and indirect, of many individuals who have contributed to the material in this paper. Thanks are due to Wayne A Sisson of the American Viscose Corporation for numerous special rayon samples, and to H Hofmann of American Bemberg Corporation for several cuprammonium rayons. Numerous fiber cross sections were prepared by the Microscopic Unit and samples of decrystallized cotton furnished by the Colloidal Properties Unit of the Cotton Fiber Section of this Laboratory.

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BOOK REVIEW

GRUNDLAGEN DER TEXTILVEREDLUNG

By M Peter, Diploma Chemist, Riehen, Switzerland, 7th completely revised edition constituting Part T61 of "Handbuch fuer Textilingenieure und Textilpraktiker" from the Dr Spohr-Verlag, Wuppertal-Elberfeld, Germany, 1956. Pp, 312 + XI. Price, DM 9.

In the pocket-fitting "Principles of Textile Finishing" Dr Spohr has published the most convenient and smallest, yet most-complete-for-its-size, preparing, dyeing, and finishing manual your reviewer has yet seen in any language. This small book of 323 pages—including 47 pp of advertising interspersed in the final supplies section—is only 4⅞" x 6⅞" on its face and ⅝" thick. It therefore fits readily into the pocket of a man's jacket or even into his hind trousers pocket. This completely revised volume constitutes the seventh edition since 1944, certainly evidence of considerable success.

The author, Herr M Peter, must be commended for having encompassed so much new and significant material into such comparatively small space. And this was done with the use of readable type — probably 8-point — and without loss of clarity of exposition.

The book at the same time contains 97 small illustrations, which, because they are predominantly simple line drawings, show clearly the principles of the various modern machines that are explained in the text for the preparation and finishing of textiles. Such types of equipment are included, among many others, as hot-flue and drum dryers; tenter frames and singeing machines; dyeing machines of the Standfast, Barotor, pad-roll (Swedish Rydbohohn Co), closed-kettle, closed-jig, and circulating types; continuous pad-steam and Williams dyeing ranges; package machines, kiers, closed jigs, and closed kettles; shearing, brushing, calendering and sanforizing machines; and roller and screen printing machines.

In the body of the manual the author gives briefly the preparation, dyeing, printing, and finishing of virtually all kinds of textiles, including those made from the old natural fibers, those made from the new all-synthetic fibers, such as acrylic, modified acrylic, polyester, and polyamide fibers, and those made from regenerated cellulosic or protein fibers. Procedures are explained in principle but without full and detailed operating directions with respect to times, temperatures, and concentrations of chemicals and assistants. A succinct description of nearly any textile process is therefore to be found, from desizing or kier boiling to resin finishing, brushing, or sanforizing. The exact amount of caustic alkali, however, for preparing the vat acid of Vat Brilliant Blue 4G or for dissolving Naphthol AS-ITR will be sought in vain. For such specific information as this, the dyer must go to a shade card or circular.

Added features of the book are lists of machine, dyestuff and textile-chemical manufacturers of the principal exporting industrial countries, and a list of textile assistants and finishing agents. Products in the latter compilation are arranged alphabetically under uses. Unfortunately, so many people are now preparing lists of textile chemicals that the response from manufacturers was apparently far from complete, especially in the United States, a country where there was only one list for American products in 1933 but where such lists are now legion.

Anyone who wishes to survey quickly and conveniently methods, equipment, and principles for the preparation, coloring, or finishing of textiles will find "Grundlagen der Textilveredlung" most valuable for both direct study and reference. Especially the student, the candidate for an examination, and the ambitious beginner in the mill will like this book. The mill man will appreciate most Herr Peter's very practical hints for the avoidance of faults and mistakes in processing.

The complete table of contents in the front and the general index in the back greatly increase the usefulness of the book for reference. An index of textile assistants by name, however, should certainly have been included.—CZD

Abstracts

Effects of Changes in the Structure of Cotton Cellulose Upon the Qualities of Cotton Products

Scott, Walter M, *J Textile Inst* **47**, P235-47, April, 1956.

The lecture was devoted principally to the possibilities of improving the qualities of cotton by chemical treatments. The lecturer first described the molecular arrangement of cotton cellulose, and referred to the changes that take place during the development of the bolls on the cotton plant.

Mercerization. The Southern Regional Research Laboratory of the US Dept of Agriculture has utilized the mercerization technique to impart new qualities to cotton fabrics. By allowing cotton gauze to shrink freely and completely in a caustic soda solution, a stretchable cotton bandage is produced which has been adopted by the US Army. Heavier fabrics of the open-weave type when similarly treated become semi-elastic and appear to be suitable for coating with plastics where flexibility is desirable.

Decrystallization. If cotton cellulose is treated with ethylamine, an ethylamine-cellulose compound is formed. If the amine is later removed, the crystallinity of the cellulose will be found to be greatly reduced. This decrystallized cotton has increased extensibility and higher elastic recovery compared with untreated cotton. The process is now in the pilot-plant stage.

Esterification. When cotton yarn is reacted with acetic anhydride, the fibrous nature of the cotton is retained and its fiber strength is not impaired, while the dyeing characteristics of the cotton are progressively altered. These acetylated fibers are distinguished by exceptional resistance to rotting, retaining from 80 to 100 percent of their original strength after one year of exposure to moist soil. They also possess increased resistance to deterioration by heat. Cotton fabrics reacted with phosphoric acid are much more flame-resistant than ordinary cotton.

Etherification. Cotton which is reacted with acrylonitrile (cyanoethylation) has improved textile properties, including increased resistance to deterioration by heat and rotting, unusual dyeing properties, and increased resistance to abrasion.

Aminized cotton is produced by treating the fiber with 2-aminoethyl sulfuric acid and caustic soda and curing. Cotton so treated has greatly increased chemical reactivity owing to the presence of amino groups attached to the molecule. The affinity for direct dyes is increased, and it acquires an affinity for acid dyes as well.

Partial carboxylation is obtained by treating cotton with monochloracetic acid, followed by caustic soda. This treatment is capable of producing a fiber which is soluble in water.

The lecturer also discussed the application of chemicals capable of cross-linking with the cellulose molecule. Flame-resistant fabrics have been prepared by treatment with an emulsion of an organic polymer prepared from bromoform and triallyl phosphate, or with tetrakis (hydroxymethyl) phosphonium chloride (THPC).

Thirty-eight references to the literature are cited.—WHC

Textiles at Work

Anon, *Textile Recorder* **74**, 60-3, May, 1956.

The author gives an account of some of the exhibits at the First National Industrial Textiles Trade Fair, held in London in April, 1956.

The outstanding feature of the fair was the wide use that has been made of the newer fibers for industrial purposes, and the manner in which their outstanding chemical and physical characteristics have been exploited to meet particular requirements. Following are some of the more important new developments.

Nylon (polyamide), on account of its strength, elasticity, abrasion resistance and flexibility and its resistance to chemical and bacterial attack, is being used for ropes, conveyor belts, fire hose, aircraft tires, and filter and press cloths.

Terylene (polyester), because of its strength, low extension, heat and chemical resistance, low absorbency and good electrical insulation, finds uses for fishing nets and lines, felts in paper mills, and tapes for the electrical industry, as well as ropes and filter cloths, like nylon.

Tenasco (high-tenacity viscose), due to its high strength, is being used in tire cords. Fibro (viscose staple), because of its absorbency, finds uses in surgical gauze. The insulating properties of acetate are utilized in electrical equipment.

Courlene (polyethylene), on account of its chemical resistance, is suitable for protective clothing for chemical workers and chemical filtration, and due to its low specific gravity, non-absorbency and flexibility at subzero temperatures, is particularly suitable for ropes used in arctic waters.

Dynel (a copolymer of vinyl chloride and acrylonitrile), having high chemical resistance, is another fiber finding uses in protective clothing. It also has an advantage in that it will not support combustion.

Among other fibers exhibited at the fair were Thermovyl (polyvinyl chloride), used in filter cloths, and glass fibers, used in the electrical industry and as plastic reinforcements, and when coated and dyed, used for nonflammable decorative purposes.—WHC

Sodium Formaldehyde Sulfoxylate: Oxidation in Unsteamed Vat Prints

Rallings, F J, *Dyer* **116**, 123, July 20, 1956.

Sodium formaldehyde sulfoxylate (Formosul or Rongalite) is used as a reducing agent in vat printing because it is stable to oxidation at room temperature and becomes active only when steamed.

It frequently happens that there is a delay between the printing and steaming operations. Under certain conditions the Formosul in the print paste may decompose while the printed goods are waiting to be steamed.

The author describes an investigation of the stability of Formosul in unsteamed prints, as affected by the relative humidity of the air, the temperature, and the particular dye being printed. Five vat dyes were used in the tests. He reports as follows:

At 20% rh a print containing Caledon Pink RL had lost only 15% of the Formosul by oxidation when stored for a week at 25°C. However, at 40% rh the loss by oxidation was increased to 35%.

Under conditions of high rh, a rise of only a few degrees in temperature can produce a large increase in the rate of oxidation.

The decomposition rate was also found to be affected in different degrees by the different dyes tested.

The author recommends that if possible unsteamed vat prints should not be stored; if they must be, the storage time should be as short as possible, at rh of less than 30 and at a low temperature.—WHC

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November 5, 1956

1956 Intersectional Contest
First-prize Winner———

EFFECT OF RESIN FINISHING ON THE LIGHT FASTNESS OF VAT DYES*

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INTRODUCTION

HISTORY———During the past twenty years there have been many new finishing agents and treatments for textile fabrics developed. These types have, for the most part, been distinctly different chemically from the types used in prior years.

These new chemical types in many cases have affected the fastness properties of dyes. In some instances they are beneficial; in others harmful.

The first classic case is the development of the nitrogen-base cationic softeners, many of which in the early days destroyed the light fastness of direct dyes. At the same time some cationic agents improve their water resistance.

Later, the application of urea-formaldehyde resins to rayon fabrics was found to affect the light fastness of many direct dyes. The application of thermosetting resin finishes to cotton fabrics has shown an unfavorable effect on the light fastness of other classes of dyes (*1*).

The extensive use of thermosetting resins on cotton fabrics in recent years has made it important to know more about the extent and, if possible, the reason for the change in fading of some vat dyes after resin treatment. At this point the effect of resin treatment on the fading properties of direct colors after treatment with thermosetting resins is well known. This was studied by the Rhode Island Section of the AATCC and reported in 1953. In the work at hand the effect of resin treatment on the fading properties of thirty vat dyes in light and heavy shades on cotton has been studied. Only thirteen of the dyes were unaffected. Two of the dyes showed less fading after resin treatment than without. Of the remaining colors most showed only slightly increased fading, but several showed marked increase in fading after resin treatment. The effect was the same whether a cyclic ethylene urea resin or a methylated melamine resin was used.

The study has been extended to include the effect of change in catalyst, omission of washing after curing, variation in curing temperature, and the addition of various types of softeners and stiffeners, such as are commonly used in commercial resin finishes.

The relationship between Fade-Ometer and sunlight fading has been studied briefly.

An attempt has also been made to correlate the fading phenomena with structure of the dye.

In the last few years the use of thermosetting resins to produce crush-resistant, shrink-resistant finishes on cotton fabrics dyed with fast colors has become a very important factor commercially in the finishing of cotton goods. The recent development of "wash and wear" finishes for cotton fabrics has made the problem of light fading after resin treatment still more acute because of the higher concentrations of the thermosetting resins and the more severe curing conditions which are required. The current yardage of cotton fabrics finished with thermosetting resins is estimated to be 500,000,000 yards per year as compared with a negligible yardage prior to the war and perhaps 40,000,000 yards per year in 1949. Originally only a few dress fabrics and shirting fabrics were finished with these resins. Now we have a large percentage of the dress goods and sport shirt fabrics, flannels for a variety of end uses, work clothing, corduroys, bedspreads, and even denim fabrics finished with thermosetting resins.

Many mills which previously never

* Presented by Paul B Stam on September 15, 1956, during the Perkin Centennial at the Waldorf-Astoria Hotel, New York, NY.

applied thermosetting resins now are in production or getting into production with them. The result is that the need for understanding of the many technical aspects of resin finishing is much more acute. It is especially a problem to many who have had no previous technical background in the field. Therefore, it is of importance that general studies be made of each of the main problems of resin application to cotton.

OBJECTIVES——The purpose of this study is to investigate the effect on the light fastness of vat dyes of the types of thermosetting resins used on cotton. It is also a purpose of this study to determine the factors in the resin-treating process which determine the fading, and to learn the mechanism of the effect.

Because of the scope of the problem and its complexity this paper will serve as an introduction to a series of papers which will attempt to analyze this phenomenon. The results of preliminary experiments will be reported and proposed experiments will be outlined.

EXPERIMENTAL BACKGROUND

Although the vat dyes are regarded as the fastest dyes on cotton, recently it has been observed that some of the vat dyes lose light fastness after treatment with thermosetting resins. Brief studies of this effect have been made by some of the dye manufacturers, which have established the fading effect, but which have not revealed its nature or its extent. For example, one manufacturer has made an extensive study of a cyclic urea resin on relatively heavy dyeings of vat colors on rayon with little evidence of effect on light fastness (*2*). Two other manufacturers are known to have made similar studies on somewhat lighter dyeings which have shown a definite effect on the light fastness of many vat dyes (*3*).

Mills producing resin-finished cotton fabrics dyed with vat dyes have observed the effect in certain cases and have accordingly avoided sensitive colors as they have happened on them. Some even have observed an improvement in light fastness of certain vat dyes after resin treating. Smith (*1*, p 744) observed that certain vat yellows such as Caledon Yellow 5GS are markedly improved in light fastness. He also observed that certain dyes, such as Caledon Yellow GNS and Durindone Brown GS, show no change in light fastness after resin treatment when dyed on cellulose separately. But, he also noted that when shades are produced from combinations of these two colors and the fabric "crease-resisted, the fastness to light can be rated at little greater than zero, particularly with the predominately yellow shades." We are told that such anomalies are also observed in the trade. The result has been an awareness of the problem without either an understanding of its scope or of its fundamentals.

The light fastness of vat dyes is, in certain cases, sensitive to other agents also. The pH of the final soaping bath can be a factor. The more alkaline the bath, the more likely many vat dyes are to lose light fastness. For this reason some mills prefer to soap vat dyes on the acid side.

It has also been observed (*3*) that the light fastness of certain vat dyes is markedly reduced if the dyed fabric is treated with a thin film of paraffin wax, such as in a water-repellent. It makes no difference whether the wax is applied from a solvent or in an aqueous emulsion.

This loss of light fastness after paraffin wax treatment occurs with some of the fastest vat dyes, but the strange thing is that, when cotton fabrics dyed with these same colors are treated with urea-formaldehyde resins, the light fastness as determined by weather exposure is definitely improved. These inconsistencies of behavior make the explanation of the phenomena all the more perplexing, and make the need for an explanation all the more important.

The Rhode Island Section of the AATCC, in studying the effect of urea-formaldehyde resins on the light fastness of direct dyes, observed (*4*) that the resin treatment improves some and harms others. They observed also that the effect is related in some measure to the ratio of formaldehyde to urea in the urea-formaldehyde paste, and in certain cases dependent on the catalyst. There was no definite relation found to the conditions of application, except that washing after curing helped some. It was also indicated that the effect was not due to chemical modification of the dye molecule by the resins. The conclusion was that the effect was photochemical in some unknown manner.

One possible approach to an explanation for some of these light-fading phenomena after treatment with finishing agents is suggested in the discussion of Smith's paper (*1*) in which E I Stern pointed out that "light fastness is the property of a system, of the combination of dye and substrate. From this viewpoint much dye behavior is not anomalous. A crease-resistant treatment produces a new system, and this new system should not be expected to have the same light fastness as the untreated dye-subtrate system." K A Hilton, in the same discussion, asks, "Is it not possible that on exposure to light and air, the resin (urea-formaldehyde) may break down to yield small quantities of formaldehyde or other reducing substance? A dyeing of Caledon Yellow G treated with a urea-formaldehyde precondensate and dried (not baked) will be found to change to a green on exposure to light more rapidly than an untreated dyeing."

Recent publications of Szwarc (*5*) point out that free methyl radicals produced by decomposition of materials containing methyl groups will react with quinones and other multiring aromatic compounds. The greater the rate of these reactions, the larger the aromatic compound (*6*). The assumption is that methyl radicals released by light from the finishing compositions, such as the resins or the paraffin, could react with the dye molecules, modifying either the auxochromic grouping or the chromophoric grouping itself, destroying the light-producing properties of the molecules. One suggestion is that the free methyl radicals can react with the quinoid group on the vat dye molecule, changing it to a methoxyl group and destroying its chromophoric structure.

This type of explanation is, obviously, incomplete as it does not explain the improvement in light fastness of certain vat dyes by urea-formaldehyde when the same dyes experience loss in light fastness after treatment with a paraffin coating on the fabric. There is, of course, possible reconciliation if, on certain molecules, the methyl radicals add in a way to stabilize the structure and on others in a way to destabilize the structure.

It is interesting, however, that Szwarc has found that the more fused rings there are in a molecule and the greater the chain of fused rings, the more likely the free radicals are to react with the molecule, provided there is no steric hindrance.

Another phenomenon which could have a bearing is that known as "radiation antagonism" (*7*), the phenomenon in which incident radiation of one wave length range in the spectrum counteracts the effect of wave lengths in another section of the spectrum to decompose or cause the dye to fade. In this phenomenon, if the countering wave length is removed by filtering action, the destructive wave lengths

TABLE I
List of vat dyes used

Code No.	Dyestuff	Colour Index or Prototype No.	Effect of Resin*
1	Anthraquinone Vat Yellow (Flavone) GC	Pr 9	0
2	Anthraquinone Vat Yellow 3R	Pr 452	–
3	Anthraquinone Vat Yellow 5GLL	– –	– –
4	Anthraquinone Vat Golden Orange 3G	Pr 290	– –
5	Anthraquinone Vat Golden Orange RRT	*CI* 1098	+
6	Anthraquinone Vat Brilliant Orange RK	Pr 116	0
7	Anthraquinone Vat Brown VR	– –	–
8	Anthraquinone Vat Brown R	*CI* 1151	–
9	Anthraquinone Vat Brown BR	Pr 118	–
10	Anthraquinone Vat Khaki 2G	Pr 122	0
11	Thioindigoid Vat Pink FF	Pr 109	0
12	Anthraquinone Vat Red FBB	Pr 296	– – –
13	Anthraquinone Vat Rubine R	Pr 124	0
14	Anthraquinone Vat Brilliant Violet 3B	Pr 288	0
15	Anthraquinone Vat Brilliant Violet 4R	*CI* 1104	–
16	Anthraquinone Vat Violet VN (FFB)	*CI* 1163	–
17	Anthraquinone Vat Violet RK (AR)	*CI* 1135	–
18	Anthraquinone Vat Blue BCS	*CI* 1113	–
19	Anthraquinone Vat Dark Blue BR (BO)	*CI* 1099	0
20	Anthraquinone Vat Navy Blue RA	*CI* 1100	+
21	Thioindigoid Vat Blue GR (Hydron Blue R)	*CI* 969	–
22	Anthraquinone Vat Jade Green (Supra type)	*CI* 1101	–
23	Anthraquinone Vat Olive Green B	Pr 293	0
24	Anthraquinone Vat Olive R	*CI* 1150	–
25	Anthraquinone Vat Olive T	Pr 547	0
26	Anthraquinone Vat Gray R	– – –	0
27	Anthraquinone Vat Gray 2G	– – –	0
28	Anthraquinone Vat Direct Black 3G	– – –	0
29	Anthraquinone Vat Direct Black RB	Pr 289	–
30	Anthraquinone Vat Black B (Chlorinated type)	*CI* 1102	0

*Legend: 0 No effect. – – Appreciable loss. + Improvement. – – – Bad loss. – Slight loss.

TABLE II
Dyes used in resin process study

Code No.	Dyestuff	Colour Index No.	Effect of Resin*
3	Anthraquinone Vat Yellow 5GLL	– –	– –
4	Anthraquinone Vat Golden Orange 3G	Pr 290	– –
5	Anthraquinone Vat Golden Orange RRT	*CI* 1098	+
6	Anthraquinone Vat Brilliant Orange RK	Pr 116	0
8	Anthraquinone Vat Brown R	*CI* 1151	–
11	Thioindigoid Vat Pink FF	Pr 109	0
12	Anthraquinone Vat Red FBB	Pr 296	– – –
26	Anthraquinone Vat Gray R	– –	0
27	Anthraquinone Vat Gray 2G	– –	0

*Legend: 0 No effect. – – Appreciable loss. + Improvement. – – – Bad loss. – Slight loss.

will then take effect and cause fading of the dye. It is possible that superficial finishes, such as the paraffin wax film or the resin treatment, could cause filtering of a protective or countering section of the spectrum of the incident light.

EXPERIMENTAL PROGRAM

It has been our objective in this study to survey the effect of the two principal types of thermosetting resins used on cotton on a representative range of vat dyes in light and medium shades. A dimethylol ethylene urea resin and an unmethylated melamine resin were selected. For a preliminary survey, thirty vat dyes were chosen with respect to importance in a representative range of colors. These dyes are listed in Table I. As it had been observed that the lighter the shade, the more pronounced the effect on the light fastness of vat dyes, the dyeings were made in a light and a medium shade by the pad-pigment method. The method of making the dyeing and the method of applying the resin are described under the heading, Experimental Procedure.

Based on the preliminary survey, a group of dyes was selected, including some which were relatively badly affected in light fastness and some which were not affected at all by the resin treatment. These are listed in Table II. These dyes were used in running further experiments to determine what factors, if any, in the resin-treating process or in the resins themselves, caused the fading.

Experiments were set up to check the following points:

1) Effect of the characteristic $-NCH_2OH$ group in the resins.
2) Effect of catalyst type.
3) Effect of free formaldehyde.
4) Effect of curing temperature.
5) Effect of alkali in the fabric.
6) Possibility of chemical reaction of the resin with the dye.
7) Effect of the resins without curing.

The experiments to determine the effect of the $-NCH_2OH$ group in the resins were made by treating the fabric with monomethylol urea and catalyst and with dimethylol urea and catalyst. These were then compared with the experiments with the same dyes on fabric finished with the dimethylol ethylene urea resin and the melamine resin.

The experiments to study the effect of the catalyst were made by running the melamine resins and the dimethylol ethylene urea resins both with a latent amine hydrochloride catalyst and an inorganic catalyst, magnesium chloride, and by running the same catalysts alone on the dyed fabric at the curing temperature. Formaldehyde was run with an amine catalyst and cured.

The effect of curing temperature was determined by curing the resin-treated fabrics both at 140°C and 180°C for 70 seconds. This was done both with the organic amine catalyst and the inorganic catalyst.

The effect of alkali in the fabric was determined by noting whether there was any difference in fading before and after washing the cured fabric in an alkaline bath. The cured fabric was washed at a pH of about 8.5 so that the fabric was left definitely more alkaline after drying than it was after curing.

The possibility of reaction of the resin with the dye to form a new chemical compound was determined by stripping the resin from the fabric, using the usual hydrochloric acid stripping procedure. Fading tests were then run on the stripped fabric.

An experiment was also run to determine whether there was correlation between Fade-Ometer fadings and outdoor exposure with and without glass over the exposed fabric in dry weather only. The outdoor exposures were correlated with the Fade-Ometer in the usual manner with test papers.

Experiments were also run to determine whether the presence of the resin monomer as a chemical composition would cause the same degree of fading without being reacted with the fiber. This was accomplished by applying the resin monomer and air drying without a catalyst present.

To obtain information of practical interest, we ran a set of experiments in which the dimethylol ethylene urea was applied with catalyst plus a softener, plus a silicone emulsion and plus a silicone emulsion with a thermoplastic resin emulsion. This was done on a small group of dyeings.

EXPERIMENTAL RESULTS

The preliminary survey showed no significant difference in the effect of the two resins, indicating that the effect is due to some factor in the method of application of the resin or to some common properties of the resin. Accordingly the further experiments (described in general terms above) were carried out in an attempt to determine the destructive factor.

The preliminary survey shows that fifteen of the dyes lost light fastness to some significant degree. Of these, three lost one or more full steps in fastness, based on the International Standard Gray Scale. The dye most affected was Anthraquinone Vat Red FBB. Anthraquinone Vat Yellow 5GLL and Anthraquinone Vat Golden Orange 3G were only somewhat less affected. Of the remaining fifteen dyes, two, Anthraquinone Vat Golden Orange RRT and Anthraquinone Vat Navy Blue RA, showed slight improvement in light fastness after resin treatment. The remaining dyes were not significantly affected.

Figures 1, 2, and 3 illustrate the results of exposure tests. One dye, Anthraquinone Vat Navy Blue RA, was improved in light fastness after resin treatment; another, Anthraquinone Vat Gray R, showed no change in light fastness after resin treatment; and another, Anthraquinone Vat Golden Orange 3G, showed slight loss in light fastness after resin treatment. It will be noted that the last color actually "fades dark" in the illustrations. This is the case on the fabric. The photography of these faded strips is very difficult and success is dependent on the particular color. Some colors photograph more readily than others in black and white. It was not found possible to get adequate contrast in colored photographs. In these pictures the pieces marked E represent the dimethylol ethylene urea, M represents the unmethylated melamine resin, and C represents the untreated control.

The experiments which have been performed thus far indicate, very definitely, that the light fading effect produced on vat dyes by thermosetting resins is due to the presence of the $-NCH_2OH$ group. The effect is a function of the concentration and possibly also of the activity of the group in the particular molecule in which it is contained. The higher the concentration of the molecule containing the group, the more the effect as shown by doubling the concentration of either the dimethylol ethylene urea resin or the melamine resin. However, when the group is present in a molecule which will give it less activity, such as in the monomethylol urea and in the dimethylol urea, it does not have as pronounced an effect. This is fairly obvious because the dimethylol ethylene urea and the melamine resin are much more reactive molecules through the $-NCH_2OH$ group in crosslinking cellulose than is dimethylol urea. The fact that there is a reduction in fading if the resin-treated fabrics are washed after curing, particularly with the highest concentrations of the resins, is further substantiation of the effect. It can be assumed that washing removes unreacted resin or water-soluble polymer. One inconsistency is that the only dye affected by monomethylol ethylene urea, as reported above, was the Anthraquinone Vat Red FBB, whereas this dye was not particularly affected by dimethylol urea; but the Anthraquinone Vat Golden Orange 3G was definitely affected and certain of the other sensitive dyes were somewhat less affected.

Apparently, whatever reaction does occur between the resin and the dye is not resistant to stripping, as the dyes show only normal fading if the resin is stripped off. This shows only that the dyes are not permanently affected by the reaction of the resins on the dyed fiber. It is quite possible that the resin monomers can react with the dyes in some manner changing the chromophoric or the auxophoric groupings through a linkage which is broken by the hydrochloric acid stripping treatment. Reaction of the resin with the dye in such a manner is a possibility because there is a slight change of shade in some cases, especially the Anthraquinone Vat Red FBB. This is the dye most affected. More positive experimental evidence will be necessary to support such a conclusion.

Another very interesting point is that neither the dimethylol ethylene urea resin nor the melamine resin requires curing to cause the light-fading effect. The presence of the catalyst does not increase the effect very much. It was found that the resins applied to the dyed fabric caused about the same fading air dried at room temperature without catalyst as with catalyst dried at room temperature or with catalyst dried at high temperature and cured (Table VII). This shows that the $-NCH_2OH$ group alone must in some way or other provide a means of making the sensitive vat dyes able to lose their chromophoric groupings or the auxochromic groupings.

The effect is definitely not due to catalyst as neither catalyst alone produced the increased fading. There was no difference between either catalyst in the degree of fading when they were used in combination with the resins. An increasing of the curing temperature had no significant effect.

Washing after curing has given some anomalous results. This wash was not strongly alkaline, being carried out in water at pH about 8.5 with a nonionic detergent. However, it was sufficiently alkaline so that it should have made the cloth more alkaline by removing acid catalyst. This would also remove the water-soluble by-products of the resin curing, and in the case of the dimethylol ethylene urea resin, it would remove any polymer produced as the polymer of this product is water soluble insofar as it has not reacted with the fiber. In the case of the melamine resin, the polymer would be, for the most part, water insoluble and would only be removed insofar as the surface resin is not firmly fixed. In general, washing improved the light fastness of the resin-treated fabric. Normally alkaline treatment does reduce the light fastness of many vat dyes. At the high concentration of the dimethylol ethylene urea resin, washing did reduce the light fastness of the Thioindigoid Vat Pink FF and of the Anthraquinone Vat Grey R.

Formaldehyde applied with catalyst and cured showed no effect on the light fastness of the dyes. This is in contrast to the observation of the Rhode Island Section Paper, which reported on the Effect of Resins on the Light Fastness of Direct Dyes (*4*).

What the mechanism is can only be conjectured at this point. However, we now have a basis for devising experiments capable of unravelling the mechanism of this reaction.

Attempts to correlate the effect of the resins on light fastness of the dyes with the structure of the dyes has been without success, as there are dyes of similar structure, which in one case are unaffected and in another case affected. For example, Anthraquinone Vat Khaki 2G and Anthraquinone Vat Brown R are both dianthrimides. The first is unaffected whereas the second loses light fastness slightly after resin treatment. Attempts to correlate other possible changes in the dye molecules on the fiber by the resins, such as interference with hydrogen bonding, also were without success.

The results of outdoor exposure tests as shown in Table VIII correlated with the Fade-Ometer test results in a general way. The exposures made under plate glass showed

slightly less fading than those exposed uncovered, in a number of cases. In the uncovered outdoor exposure tests the resin-treated specimens tended to show a slight improvement over the controls in colors which have been reported as not affected or only slightly reduced in fastness after Fade-Ometer exposure. This correlates, in some measure, with the information reported above that urea-formaldehyde treatment improves the light fastness of certain vat dyes on exposure to the weather (*3*). Another difference found on these tests is that four of the nine dyes included were more affected adversely by the dimethylol ethylene

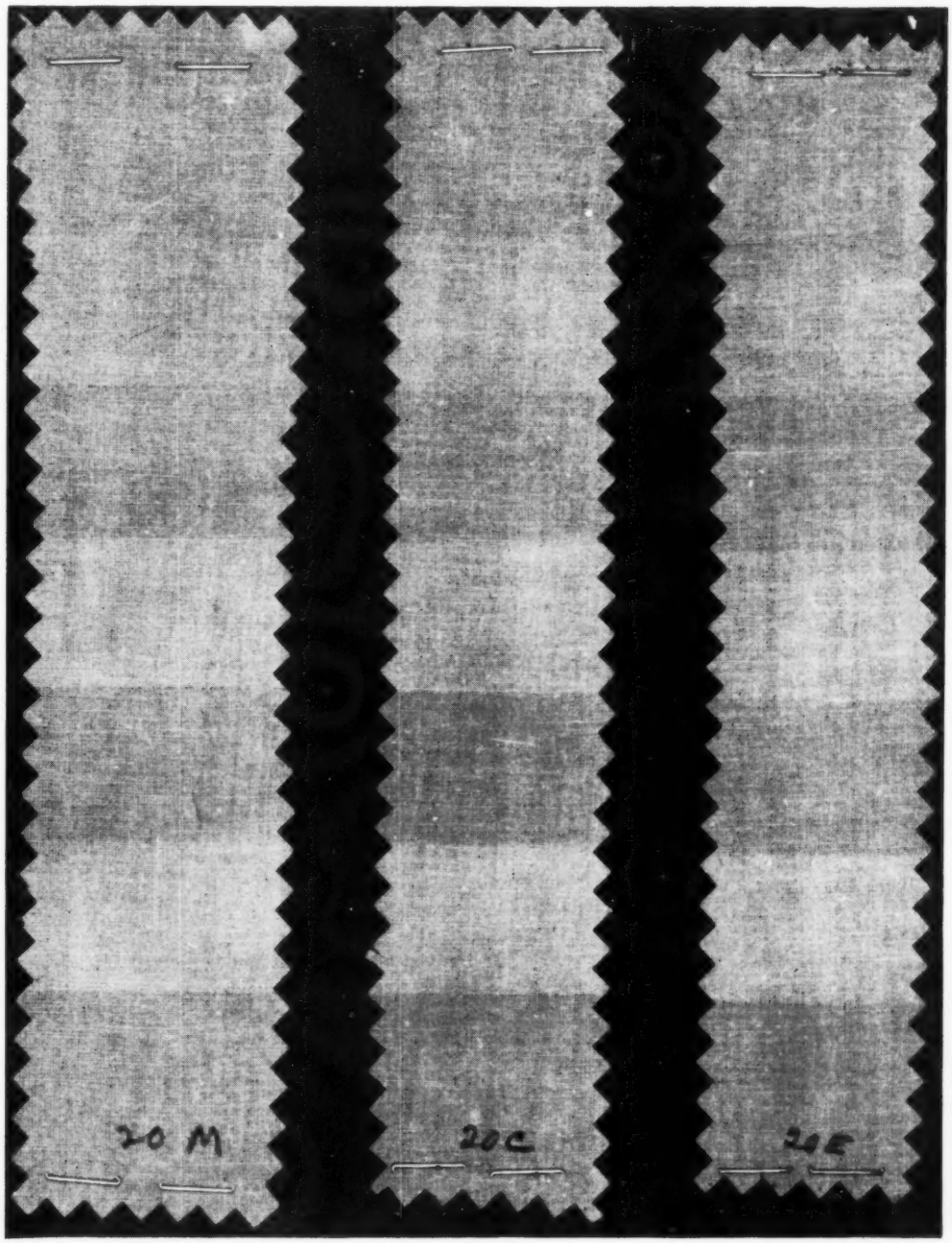

Figure 1
2% Anthraquinone Navy Blue RA

urea resin than by the melamine resin. This is the first case where a definitely noticeable difference has been found between the two resins.

Our tests, designed for practical information, showed that the cationic softener, the silicone emulsion and the thermoplastic copolymer had no significant effect on the light fastness over and above the effect of the thermosetting resin itself, except in the cases of Thioindigoid Vat Pink FF, and Anthraquinone Vat Red FBB. In both cases the cationic softener and the silicone emulsion reduced the light fastness one full step beyond the effect of the resin itself. Pink FF, which of itself fades badly, is not affected by

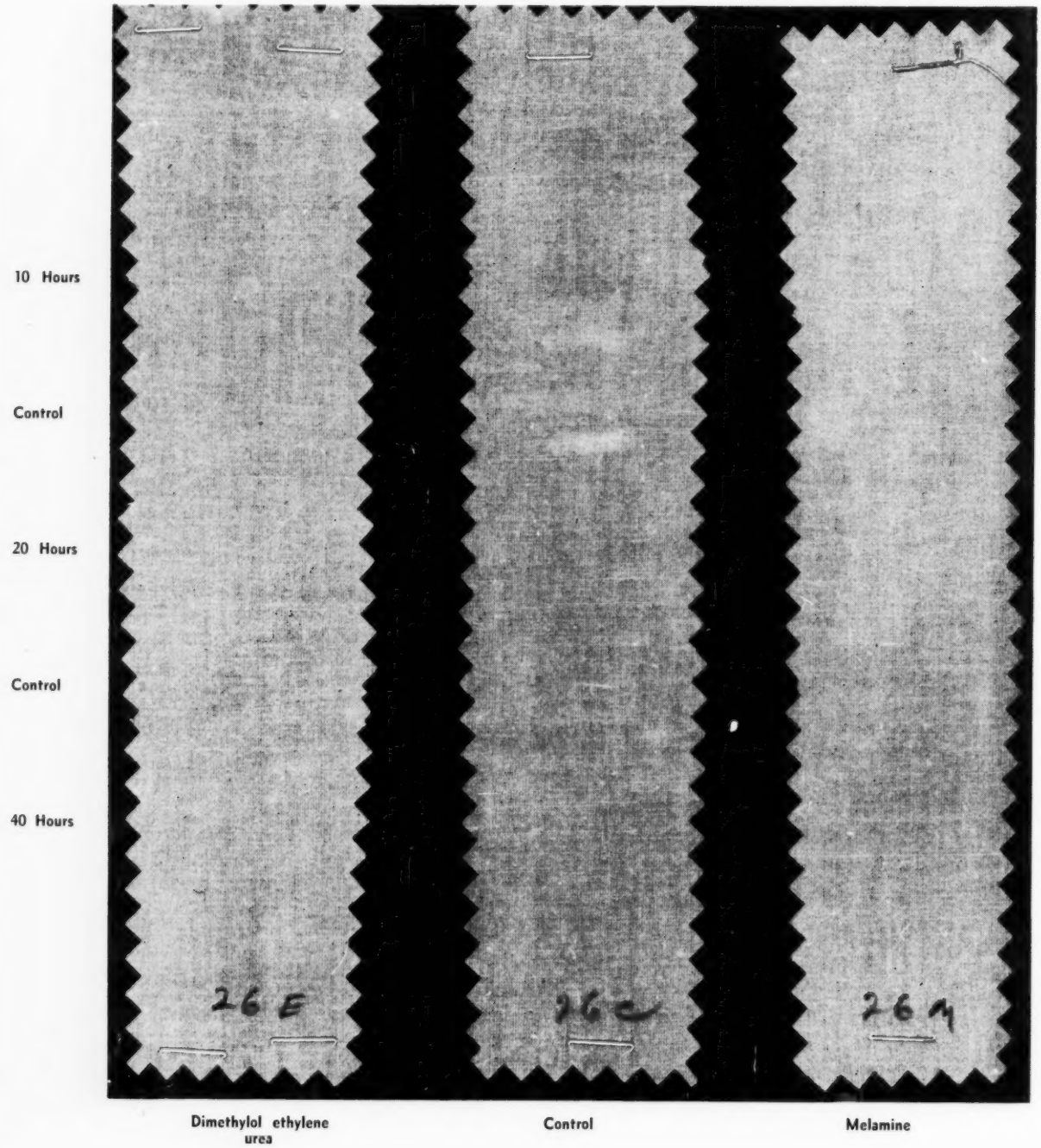

Figure 2
2% Anthraquinone Vat Gray R

the resin, so the effect may be due solely to the cationic softener. Silicones are generally emulsified with cationic surfactants. This may explain the effect of the silicone. It is not surprising that the Anthraquinone Vat Red FBB is affected as it is the most sensitive color with respect to effect of resins. It is possible, of course, that in its case, the cationic softener and the cationic emulsifier in the silicone emulsion accentuate the effect of the resin or are additive on to the effect of the resin. The thermoplastic copolymer showed no additional effect over and above that of the silicone emulsion when combined with it.

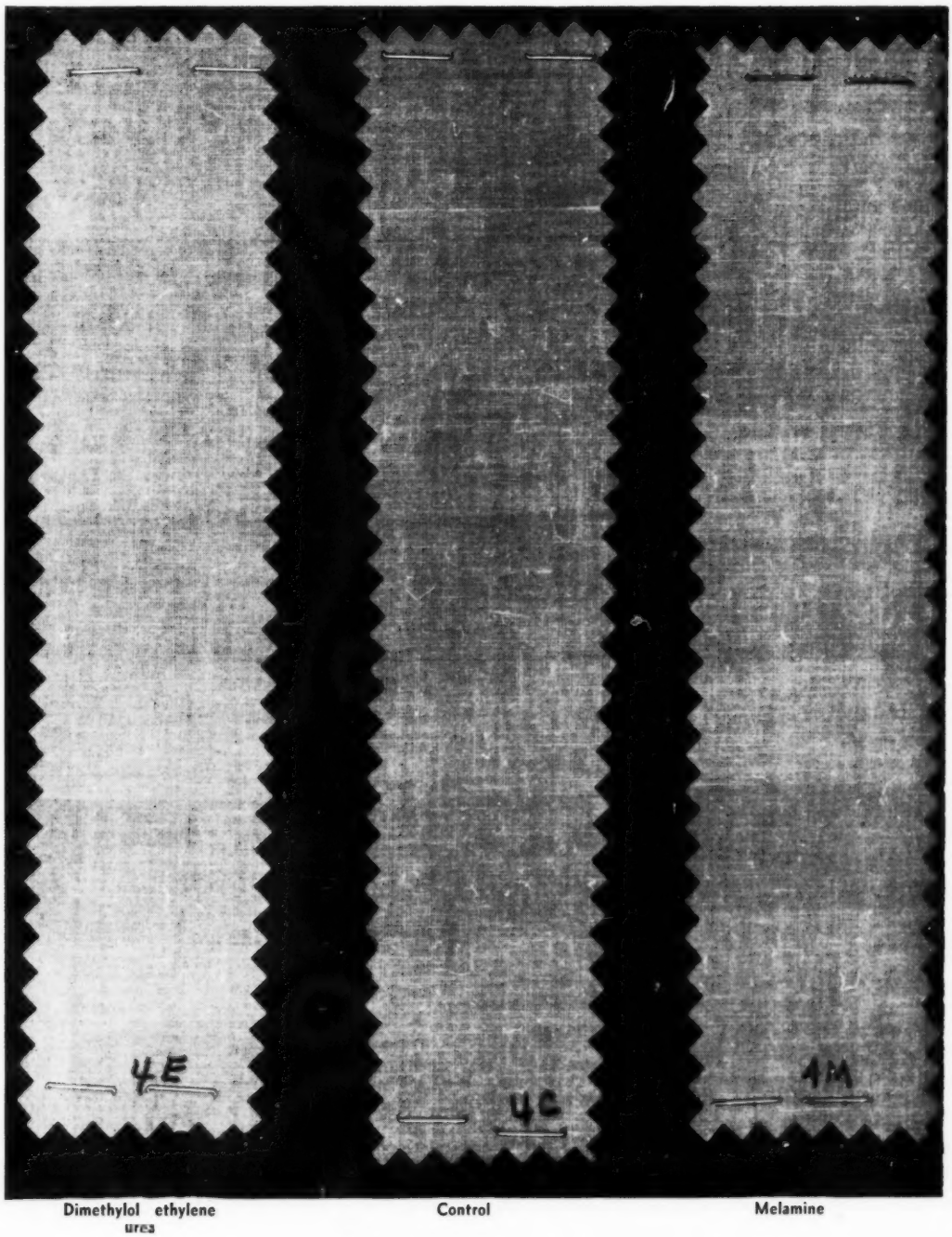

Figure 3
0.25% Anthraquinone Vat Golden Orange 3G

PROPOSED EXPERIMENTS

There are many additional experiments which come to mind in as complex a phenomenon as this has proven to be. It is our intention to follow up on some of the obvious leads at the beginning so as to establish a more firm experimental basis with our present information. Then we will attempt experiments further afield designed to get more directly at the fundamentals of the problem.

We have proposed the following aspects of the problem for study:

1) Study of additional vat dyes to search for more colors which are affected favorably or unfavorably in light fastness by resin treatment. This should give a better basis for correlation with structure, or serve as a basis for explanation of the phenomenon in terms of some reaction such as that discovered by Szwarc (*5*).

2) Study of catalysts which are not chlorides. The two catalysts used thus far were chlorides.

3) Study of the effect of the resins on the same dyes with cellophane as the substrate. This will provide a more ready means of determining whether there is a change in the absorption spectrum of the dye when treated with the resin. These experiments will include some in which one layer of cellophane treated with the resin is placed over a layer of cellophane containing the dye. In this way it will be possible to determine whether absorption of part of the spectrum by the resin changes the light fastness of the dye.

4) A study will be made of the effect of resin treatment on the fading of dyeings from mixtures of dyes which do and do not lose light fastness after resin treatment. It has been indicated, as pointed out by Smith (*1*), that dyes which are unaffected in light fastness by resin treatment when dyed alone lose this resistance when dyed together and resin treated.

5) The effect of long-term exposure on the dyes which were unaffected at 40 hours after resin treatment will be determined. They will be exposed 80-120 hours. This will indicate whether the effect is one of fundamental difference in the dye structure or solely a matter of degree in terms of exposure time.

6) Further study of the effect of alkali in the fabric will be made to make certain whether the differences found, in which some dyes were improved and others hurt, are purely a matter of washing out harmful by-products from the resin curing or definitely of alkalinity. Some of the dyes which showed loss in light fastness after resin treatment will be thoroughly washed on the acid side to determine whether there is a change in loss of light fastness after resin treatment.

7) There will be an additional study made of the effect of resin concentration on the degree of fading, including application of much higher concentrations of monomethylol urea; also other resin types, such as methylated melamine, methylated urea resins and possibly nylon, type 8, which is a $-NCH_2OH$ compound. This will tie down more closely the relationship of the $-NCH_2OH$ group to the fading phenomenon.

8) A study will be made to determine whether the method of dyeing has an effect on the fading phenom-

TABLE III

Resin application experiments performed to study process variations

Table	Code	Experiment
		I. Effect $-NCH_2OH$ Group
VI	U-1	10% monomethylol urea formaldehyde (43%)/ amine hydrochloride catalyst, cured 170°C, not washed.
VI	U-2	U-1 washed.
VI	U-3	10% monomethylol urea formaldehyde/$MgCl_2$ catalyst, cured 170°C, not washed.
VII	D-1	10% solids dimethylol urea plus 1% amine hydrochloride catalyst, cured 180°C, not washed.
VII	D-2	D-1 washed.
IV	M	7.5% melamine resin/1% amine hydrochloride catalyst, cured 180°C, 70 sec, washed.
IV	E	10% dimethylol ethylene urea/1% amine hydrochloride catalyst, cured cured 180°C, 70 sec, washed.
VII	M-12	15% melamine resin plus 1% amine hydrochloride catalyst, cured 180°C, not washed.
VII	E-16	20% dimethylol ethylene urea plus 1% amine hydrochloride catalyst, cured 180°C, not washed.
VII	E-17	E-16 washed.
		II. Effect of Catalyst Type
V	M-5	7.5% melamine resin plus 1.5% $MgCl_2 \cdot 6H_2O$ (50%) catalyst, cured 180°C, 70 sec, washed.
V	E-5	10% dimethylol ethylene urea plus 1.5% $MgCl_2 \cdot 6H_2O$ (50%) catalyst cured 180°C, 70 sec, washed.
V	AC	1% amine hydrochloride catalyst, cured 180°C, for 70 sec, not washed.
V	Mg	1.5% $MgCl_2 \cdot 6H_2O$ (50%) catalyst, cured 180°C, 70 sec, not washed.
		III. Effect of Free Formaldehyde
V	F	5% Formalin, cured 180°C, 70 sec, not washed.
		IV. Effect of Curing Temperature
V	M-1	7.5% melamine resin/amine hydrochloride catalyst, cured 140°C, not washed.
V	M-2	M-1 washed.
V	M-3	Melamine resin/amine hydrochloride catalyst, cured 180°C, not washed.
V	M-4	M-3 washed.
V	M-5	Melamine resin/$MgCl_2$ catalyst, cured 180°C, washed.
V	E-1	Dimethylol ethylene urea/amine hydrochloride catalyst, cured 140°C, not washed.
V	E-2	E-1 washed.
V	E-3	E-1 cured 180°C, not washed.
V	E-4	E-3 washed.
		V. Effect of Alkali in the Fabric
		Compare effect of washed and unwashed treatments.
		VI. Possibility of Chemical Reaction of the Resin with the Dye
VI	M-6	7.5% melamine resin plus 1% amine hydrochloride catalyst, cured 140°C, 70 sec, not washed.
VI	M-7	M-6 stripped by 1% HCl 80°C, 30 min.
VI	M-8	7.5% melamine resin plus 1.5% $MgCl_2 \cdot 6H_2O$ (50%) catalyst.
VI	M-9	M-8 stripped.
VI	E-10	10% dimethylol ethylene urea plus 1% amine hydrochloride catalyst, cured 140°C, 70 sec, not washed.
VI	E-11	E-10 stripped.
VI	E-12	10% dimethylol ethylene urea plus 1.5% $MgCl_2 \cdot 6H_2O$ (50%) catalyst.
VI	E-13	E-12 stripped.
VI	S	No resin and stripping treatment.
		VII. Effect of the Resins Without Curing
VII	M-10	7.5% melamine resin, air dried, not washed.
VII	M-11	1% amine hydrochloride catalyst, air dried, not washed.
VII	E-14	10% dimethylol ethylene urea, air dried, not washed.
VII	E-15	10% dimethylol ethylene urea plus 1% amine hydrochloride catalyst, air dried, not washed.

TABLE IV

Preliminary evaluation of the effect of dimethylol ethylene urea and melamine resins on the light fastness of common vat dyes

Code no. of dye	Time of exposure in Fade-Ometer								
	10 hours			20 hours			40 hours		
	C	E	M	C	E	M	C	E	M
1-L	3	3	3	2	2	2	1	1	1
1-H	4/3	4/3	4/3	3	3	3	2	2	2
2-L	4/5	4/5	4/5	4/5	4	4	4/5	4	4
2-H	5	4/5	4/5	5	4/5	4/5	4/5	4	4
3-L	5/4	4/3	4/3+	4	3	3+	4/3	3/2	3/2+
3-H	5	4	4+	5/4	4/3	4/3+	4	3/2	3/2+
4-L	5/4	4/3	4/3	4	3	3	4/3	3/2	3/2
4-H	5	3	3	4	3/2	3/2	4/3	2	2
5-L	4	4+	4+	4/3	4	4	3	4/3	4/3
5-H	5/4	5/4+	5/4+	4	4+	4+	4/3	4/3+	4/3+
6-L	4	4	4	4/3	4/3	4/3	3	3+	3+
6-H	5/4	5/4	5/4	5/4	5/4	5/4	4	4	4
7-L	4	4/3	4/3-	4/3	3	3-	3	3/2	3/2-
7-H	4	4/3	4/3-	4/3	3	3-	3	3/2	3/2-
8-L	5	5/4	5/4	5/4	4	4	4	4/3	4/3
8-H	5	5/4	5/4	5	4	4	5/4	4/3	4/3
9-L	5	5/4	5/4	5/4	4	4	4	4/3	4/3
9-H	5/4	5/4	5/4	5/4	5/4	5/4	4	4/3	4/3
10-L	5	5	5	5	5	5	5/4	5/4	5/4
10-H	5	5	5	5	5	5	5/4	5/4	5/4
11-L	3	2	1	3	2	1	3	2	1
11-H	4	3	2	4	3	2	4	3	2
12-L	4	3	3	4/3	2	2	3	1	1
12-H	5/4	3	3	4	2	2	3	1	1
13-L	5/4	5/4	5/4	4	4	4	3	3	3
13-H	5	5	5	5	5	5	5/4	5/4	5/4
14-L	4	4/3	4	4/3	3	4/3	3	3/2	3
14-H	5/4	4	5/4	4	4/3	4	4/3	3	4/3
15-L	4	4/3	4-	4/3	3	4/3-	3	3/2	3-
15-H	5/4	5/4	5/4	4	4	4	4/3	4/3	4/3
16-L	4/3	4/3	4/3	3	3	3	3/2	3/2	3/2
16-H	5/4	4	4	4	4/3	4/3	4/3	3	3
17-L	4	4/3	4	4/3	3	4/3	3	3/2	3
17-H	5	5/4	5/4	5/4	4	4	4	4-	4-
18-L	5	5/4	5/4	5/4	5/4	5/4	5/4	4	4
18-H	5	5	5	5	5/4	5/4	5	4	4
19-L	4/3	4/3	4/3	3	3	3	3/2	3/2	3/2
19-H	5	5/4	5/4	4	4-	4-	4/3	4/3-	4/3-
20-L	3	3	3	2	2	2	1	1	1
20-H	4	4+	4+	4/3	4/3+	4/3+	3	3+	3+
21-L	4/3	3	3	3	3/2	3/2	3/2	2	2
21-H	4	4/3	4/3	3	3/2	3/2	3/2	2	2
22-L	4	4	4	4/3	4/3	4/3	4/3	4/3	4/3
22-H	5	5	5	5	5/4	5/4	5/4	4	4
23-L	5	5	5	5	5	5	5/4	5/4	5/4
23-H	5	5	5	5	5	5	5	5	5
24-L	5	5/4	5/4	5/4	5/4	5/4	5/4	4	4
24-H	5	5/4	5/4	5/4	4	4	4	4/3	4/3
25-L	5	5	5	5/4	5/4	5/4	5/4	5/4	5/4
25-H	5	5	5	5	5/4	5/4	5	5/4	5/4
26-L	5	5	5	5	5	5	5	5/4	5/4
26-H	5	5	5	5	5	5	5/4	5/4	5/4
27-L	5/4	5/4	5/4+	4	4	5/4	4/3	4/3	4
27-H	5	5	5	5/4	5/4	5/4	5/4	5/4	5/4
28-L	5/4	5/4	5/4	4	4-	4	4/3	4/3-	4
28-H	5	5	5	5	5	5	5	5/4	5-
29-L	5/4	4	4	4	4/3	4/3	4/3	3	3
29-H	5-	5/4	5	5/4	4	4+	4	4/3	4/3+
30-L	4	4-	4-	4/3	3	3	3	3-	3-
30-H	5	5	5	5	5	5	5/4	5/4	5/4

L = light shade (0.25%), H = heavy shade (2.0%)
C = control, no resin treatment
E = ethylene urea resin
M = melamine resin
For key to names of dyes see Table I.

enon after resin treatment. It has been reported that a very carefully made dyeing will show less fading.

9) An attempt will be made to follow up the Scwarz reaction by determining whether free methyl radicals produced chemically rather than photochemically will promote fading. If this does promote fading, and there is a correlation in the dye affected with the results reported in our experiments here, it will be in order to determine experimentally whether free methyl radicals can be produced photochemically by resins on treated cotton fabrics.

10) It may also be indicated to study the effect of changing the fiber to one of a different chemical type or of a closely related chemical type, such as regenerated cellulose rayon.

EXPERIMENTAL PROCEDURE

DYESTUFFS AND DYEING PROCEDURE——Table I lists the thirty dyes used in the preliminary survey with the identifying code numbers used in the tables reporting fastness tests. The effect of resin treatment on the light fastness of the dyes is indicated on the table as follows:

No effect 0
Improvement +
Slight Loss -
Appreciable Loss - -
Bad Loss - - -

Table II lists the nine dyes used in the experiments to study the various factors in the application of the resins which might determine the effect on fading. The group was selected to include dyes improved, dyes unaffected and dyes harmed in light fastness by the resins. Due to shortage of the dyed fabrics, the light dyeings were used in some cases and the heavy dyeings in other cases. In certain cases one or more dyes has had to be omitted because of lack of dyed fabric.

The colors were arbitrarily divided into three groups and sent to three laboratories for dyeing on 80 x 80 cotton print cloth. The arbitrary division was made as follows: Laboratory I—dyes 1, 4, 7, 10, 13, 16, 19, 22, 25, 28; Laboratory II—dyes 2, 5, 8, 11, 14, 17, 20, 23, 26, 29; Laboratory III—dyes 3, 6, 9, 12, 15, 18, 21, 24, 27, 30.

Two dyeings were made of each of the colors, namely, 0.25% (light shade) and 2.0% (heavy shade). In each case, the pigment-pad-dry-chemical pad-steam method of dyeing was used. Four pieces of cloth, each

8 inches wide and 2 yards long were padded through each dye solution. They were then suspended horizontally in air at room temperature until dry. They were developed by padding through a solution containing 4 oz/gal of caustic soda and of hydrosulfite and then immediately steamed for 30 seconds at 218-220°F. They were rinsed in cold water and then oxidized for 10 minutes at 130°F in a bath containing 2 grams/liter of sodium perborate. Finally, the pieces were scoured for 10 minutes at the boil in a bath containing 1 g/l of alcohol sulfate detergent and 1.5 g/l of tetrasodium pyrophosphate. They were subsequently rinsed hot, then cold, and soured in 0.5% acetic acid. They were ironed dry without rinsing.

RESIN TREATMENT ——— The two resins chosen for the study of the effects on light-fastness properties were a commercial melamine resin and a dimethylol ethylene urea resin specially prepared from recrystallized ethylene urea. In the preliminary work to determine which of the dyes would be most interesting for further study, 1.0%, based on the resin, of an amine hydrochloride catalyst was used. In order to make certain that the samples were completely free of alkali, just prior to padding with resin we again soured the material in 1.0% acetic acid and air dried. Three 8½-inch lengths of each dyed sample were marked with the code dye number and then padded through a 7.5% solution in the case of the melamine resin (95% solids) or a 10% solution in the case of the dimethylol ethylene urea (50% solids). The pick-up in padding was 70%. These concentrations were chosen for equal crease-resistance values, namely, about 3.2 x 3.0 TBL. After being padded, the samples were air dried and subsequently cured continuously along with a control sample for 70 seconds at 360°F. Finally, the samples were washed with 0.5% nonionic detergent in water of pH 8.5-9.0 at 120°F for 10 minutes and well rinsed. Where this procedure was changed in subsequent work, an appropriate notation is made in the keys to the tables. Experiments performed to study variations in the resin application process are in Table III.

TESTS FOR LIGHT FASTNESS ———*A. Fade-Ometer.* Following the resin treatments, which were all carried out in one laboratory, duplicate samples were mounted for light fastness tests by the conventional procedure and were forwarded to a number of laboratories for exposure in the Fade-Ometer. Efforts were

TABLE V

Effect of various modifications of resin treatment on the light-fastness of selected vat dyes

Code no. of dye	3-H			4-H			5-L		
Code no. of test	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40
Control	5	5/4	4	5	4	4/3	4	4/3	3
M-1	4	4/3	3/2	3	3/2	2	5/4	4	4/3
M-2	4	4/3	3/2	3	3/2	2	5/4	4	4/3
M-3	4	4/3	3/2	3	3/2	2	5/4	4	4/3
M-4	4	4/3	3/2	3	3/2	2	5/4	4	4/3
M-5	4	4/3	3/2	3	3/2	2	5/4	4	4/3
E-1	4/3	3	2	3	3/2	2	5/4	4	4/3
E-2	4/3	3	2	3	3/2	2	5/4	4	4/3
E-3	4/3	3	2	3	3/2	2	5/4	4	4/3
E-4	4/3	3	2	3	3/2	2	5/4	4	4/3
E-5	4/3	3	2	3	3/2	2	5/4	4	4/3
E-6	4/3	3	2	3	3/2	2	5/4	4	4/3
E-7	4/3	3	2	3	3/2	2	5/4	4	4/3
E-8	4/3	3	2	3	3/2	2	5/4	4	4/3
E-9	4/3	3	2	3	3/2	2	5/4	4	4/3
F	5	5/4	4	5/4	4	4/3	4	4/3	3
AC	5	5/4	4	5/4	4	4/3	4	4/3	3
MG	5	5/4	4	5/4	4	4/3	4	4/3	3

Code no. of dye	6-H			8-H			11-H		
Code no. of test	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40
Control	5/4	5/4	4	5	5	5/4	4	4	4
M-1	5/4	5/4	4	5/4	4	4/3	4	3	2
M-2	5/4	5/4	4	5/4	4	4/3	4	3	2
M-3	5/4	5/4	4	5/4	4	4/3	4	3	2
M-4	5/4	5/4	4	5/4	4	6/3	4	3	2
M-5	5/4	5/4	4	5/4	4	4/3	4	3	2
E-1	5/4	5/4	4	5/4	4	4/3	4	3	2
E-2	5/4	5/4	4	5/4	4	4/3	4	3	2
E-3	5/4	5/4	4	5/4	4	5/3	4	3	2
E-4	5/4	5/4	4	5/4	4	4/3	4	3	2
E-5	5/4	5/4	4	5/4	4	4/3	4	3	2
E-6	5/4	5/4	4	5/4	4	4/3	3	2	1
E-7	5/4	5/4	4	5/4	4	4/3	3	2	1
E-8	5/4	5/4	4	5/4	4	4/3	3	2	1
E-9	5/4	5/4	4	5/4	4	4/3	3	2	1
F	5/4	5/4	4	5	5	5/4	4	3	2
AC	5/4	5/4	4	5	5	5/4	4	3	2
MG	5/4	5/4	4	5	5	5/4	4	3	2

Code no. of dye	12-H			26-H			27-L		
Code no. of test	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40
Control	5/4	4	3	5	5	5/4	5/4	4	4/3
M-1	3	2	1	5	5	5/4	5/4	5/4	4
M-2	3	2	1	5	5	5/4	5/4	5/4	4
M-3	3	2	1	5	5	5/4	5/4	5/4	4
M-4	3	2	1	5	5	5/4	5/4	5/4	4
M-5	3	2	1	5	5	5/4	5/4	5/4	4
E-1	2	1	1	5	5	5/4	5/4	5/4	4
E-2	4	4/3	3	5	5	5/4	5/4	5/4	4
E-3	2	1	1	5	5	5/4	5/4	5/4	4
E-4	3	2	1	5	5	5/4	5/4	5/4	4
E-5	3	2	1	5	5	5/4	5/4	5/4	4
E-6	2	1	1	5	5	5/4	5/4	5/4	4
E-7	2	1	1	5	5	5/4	5/4	5/4	4
E-8	2	1	1	5	5	5/4	5/4	5/4	4
E-9	3	2	1	5	5	5/4	5/4	5/4	4
F	5/4	4	3	5	5	5/4	5/4	4	4/3
AC	5/4	4	3	5	5	5/4	5/4	4	4/3
MG	5/4	4	3	5	5	5/4	5/4	4	4/3

Key to colors and tests in Table Va.

TABLE Va

Identification of test code numbers shown in Table V

Test code no.	Identification
M-1	Melamine resin/amine hydrochloride catalyst, cured 140°C, not washed.
M-2	M-1 washed.
M-3	Melamine resin/amine hydrochloride catalyst, cured 180°C, not washed.
M-5	M-3 washed
M-5	Melamine resin/$MgCl_2$ catalyst, cured 180°C, washed.
E-1	Dimethylolethylene urea/amine hydrochloride catalyst, cured 140°C, not washed.
E-2	E-1 washed.
E-3	E-1 cured 180°C, not washed.
E-4	E-3 washed.
E-5	Dimethylolethylene urea/$MgCl_2$ catalyst, cured 180°C, washed.
E-6	E-3 plus cationic softener, not washed.
E-7	E-3 plus silicone water repellent, not washed.
E-8	E-3 plus silicone water repellent thermoplastic copolymer, not washed.
E-9	E-8 washed.
F	5% Formalin, cured 180°C, not washed.
AC	1% amine hydrochloride catalyst, cured 180°C, not washed.
MG	1.5% $MgCl_2$ catalyst, cured 180°C, not washed.

TABLE VI

Effect of various modifications of resin treatment on the light-fastness of selected dyes.

Code no. of dye	3-L			4-L			6-L			8-L		
Code no. of test	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40
Control	5/4	4	4/3	5/4	4	4/3	4	4/3	3	5	5/4	4
E10	4/3	3	3/2	4	4/3	3	5	5/4	4	5/4	4	4/3
E11	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
E12	4/3	3	3/2	4	4/3	3	5	5/4	4	5/4	4	4/3
E13	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
F 2	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
F 3	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
M 6	4/3	3	3/2	4	4/3	3	5	5/4	4	5/4	4	4/3
M 7	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
M 8	4/3	3	3/2	4	4/3	3	5	5/4	4	5/4	4	4/3
M 9	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
S	5/4	4	4/3	5	5/4	4	5	5/4	4	5	5/4	4
U 1	5/4	4	4/3	5/4	4	4/3	5	5/4	4			
U 2	5/4	4	4/3	5/4	4	4/3	5	5/4	4			
U 3	5/4	4	4/3	5/4	4	4/3	5	5/4	4			
U 4	5/4	4	4/3	5/4	4	4/3	5	5/4	4			

Code no. of dye	11-L			12-L			26-L			27-H		
Code no. of test	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40	Hours 10	20	40
Control	3	3	3	4	4/3	3	5	5	5	5	5/4	5/4
E10	3	2	1	4	4/3	3	5	5	5	5	5/4	5/4
E11	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
E12	3	2	1	4	4/3	3	5	5	5	5	5/4	5/4
E13	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
F 2	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
F 3	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
M 6	3	2	1	4	4/3	3	5	5	5	5	5/4	5/4
M 7	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
M 8	3	2	1	4	4/3	3	5	5	5	5	5/4	5/4
M 9	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
S	3	2	1	5/4	4	4/3	5	5	5	5	5/4	5/4
U 1	3	2	1	4/3	3	3/2	5	5	5	5	5/4	5/4
U 2	3	2	1	4/3	3	3/2	5	5	5	5	5/4	5/4
U 3	3	2	1	4/3	3	3/2	5	5	5	5	5/4	5/4
U 4	3	2	1	4/3	3	3/2	5	5	5	5	5/4	5/4

(S)—These tests were inadvertently underexposed; hence, the values shown are comparable only within this set.
Key to colors and tests in Table VIA.

TABLE VIa

Identification of test code numbers shown in Table VI

Test code no.	Identification
E10	Dimethylolethylene urea/amine hydrochloride catalyst, cured 140°C, not washed.
E11	E-10 stripped (as "S") with 1% HCl, 80°C, 30 min, liquor ratio 30/1.
E12	DME urea/$MgCl_2$ catalyst, cured 140°C, not washed.
E13	E-12 stripped with 1% HCl. 80°C, 30 min, liquor ratio 30/1.
F2	5% Formalin/amine hydrochloride catalyst, cured 140°C, not washed.
F3	F2 stripped with 1% HCl, 80°C, 30 min, liquor ration 30/1.
M6	Melamine resin/amine hydrochloride catalyst, cured 140°C, not washed.
M7	M6 stripped with 1% HCl, 80°C, 30 min, liquor ratio 30/1.
M8	Melamine resin/$MgCl_2$ catalyst, cured 140°C, not washed.
M9	M8 stripped with 1% HCl, 80°C, 30 min, liquor ratio 30/1.
S	No resin, stripped with 1% HCl, 80°C, 30 min.
U1	10% monomethylol urea formaldehyde (43% solids)/amine hydrochloride catalyst, cured 170°C, not washed.
U2	U1 washed.
U3	10% MMUF/$MgCl_2$ catalyst, cured 170°C, not washed.
U4	U3 washed.

made to have the duplicates in different machines.

The samples were exposed to 10, 20, and 40 standard Fade-Ometer hours as determined by National Bureau of Standards calibration paper. Sections B and C of the shield were not removed during the tests. Section A was exposed for 10 hours, the center section for 20 hours, and section D for 40 hours. All tests were made at least in duplicate on both the light and the heavy shades.

B. Sunlight. Two complete sets were run, one under plate glass, one not covered. Exposures were made 15° from horizontal toward the South. All exposures were made on bright or hazy days between the hours of 9:00 AM and 4:00 PM, during the months of June and July, 1956 in Raleigh, N C, in a non-industrial area.

EVALUATION OF FADING——The evaluation was conducted in all cases by a committee of three people who were experienced in this type of work. The scale used was an arbitrary scale showing relative fading with respect to the unexposed control. It roughly approximates the International Gray Scale. Our scale is rated as follows:

5—No change
4—Noticeable change
3—Appreciable change
2—Considerable change
1—Very great change

DETAILED RESULTS——Light fastness evaluations for all tests run are reported in detail in Tables IV-VIII with padding formulas used.

SUMMARY AND CONCLUSIONS

In this preliminary study, it has been established that 15 of a group of 30 representative vat dyes lose light fastness to some degree after treatment with the reactive type of thermosetting resins. The resins used were dimethylol ethylene urea and an unmethylated melamine resin. Two colors showed a slight improvement in light fastness after the resin treatment.

A careful study of this effect demonstrated that it is due to the $-NCH_2OH$ group in the resin molecule. There is a slight effect from monomethylol urea, somewhat more effect from dimethylol urea but a much more pronounced effect from the dimethylol ethylene urea and the unmethylated melamine resin. The effect is also increased with increasing concentrations of the latter resins. Furthermore, curing is unnecessary to produce the effect. The mere presence of the resin, even without catalyst, will produce the effect.

It has been definitely established that the effect is not due to catalyst nor to the curing temperature nor to the free formaldehyde which might be in the resin.

From a theoretical standpoint a basis has been established for devising experiments to determine the mechanism by which the $-NCH_2OH$ group causes certain vat dyes to become more sensitive to light fading.

Recent fundamental developments, such as the Scwarz reaction of methyl groups with anthraquinone compounds, provide a possible explanation for this reaction. From a practical standpoint, it has been established that the dyer and the finisher must take into account that certain vat dyes will show increased light fading

TABLE VII

Effect of dimethylol urea, and of dimethylol ethylene urea and melamine resin without cure and at higher concentrations.

Treatment	3L			4L			6L			8L		
Hours	10	20	40	10	20	40	10	20	40	10	20	40
D-1	5/4	4	4/3	4	4/3	3	5/4	4/3	3	5	5/4	4
D-2	4	4/3	3	4	4/3	3/2	4	3	2	5	5/4	4
E-14	3	2	1	4	3	2	4	4/3	3	5/4	4	4
E-15	4/3	3	2/1	4	4/3	3/2	5/4	4/3	3	5	5/4	4
E-16	4/3	3	2/1	4	3	2	5/4	4/3	4/3	5/4	4	4/3
E-17	5/4	4/3	3	4	4/3	3/2	4	3	2	5	5/4	5/4
M-10	4	3	2	4	4/3	3/2	4	4/3	3	5	4	4/3
M-11	4	3	2	4	4/3	3/2	4	3	3/2	5/4	4/3	4/3
M-12	4	3	2	4	3	2/1	4	4/3	3/2	4/3	3	3

Treatment	11L			12L			26L			27H		
Hours	10	20	40	10	20	40	10	20	40	10	20	40
D-1	3	3/2	2/1	4	4/3	3	5	5	5	5/4	5/4	4
D-2	3	2	1	4	4/3	3	5	5	5	5	5/4	4/3
E-14	3	3/2	2/1	4/3	3	2	5	5	5/4	5	5/4	4
E-15	4/3	3	2/1	4	4/3	3/2	5	5	5/4	5	5/4	4
E-16	4/3	3	2/1	4	4/3	3/2	5	5	5/4	5	5/4	5/4
E-17	4/3	2/1	1	5/4	4/3	3	5/4	5/4	4	5/4	4	4
M-10	3	2	1	4/3	3	3/2	5	5/4	4	5	5/4	4
M-11	3	2/1	1	4/3	3	3/2	5	5/4	4	5	5/4	4
M-12	3	2	1	3	2	2/1	5	5	5	5/4	4	4

Key to colors and tests in Table VIIa.

TABLE VIIa

Identification of test code numbers shown in Table VII

Test code no.	Identification
D-1	10% solids dimethylol urea plus 1% amine hydrochloride catalyst, cured 180°C, not washed.
D-2	D-1 washed.
E-14	10% dimethylol ethylene urea, air dried, not washed.
E-15	10% dimethylol ethylene urea plus 1% amine hydrochloride catalyst, air dried, not washed.
E-16	20% dimethylol ethylene urea plus 1% amine hydrochloride catalyst, cured 180°C, not washed.
E-17	E-16 washed.
M-10	7.5% unmethylated melamine resin, air dried, not washed.
M-11	7.5% unmethylated melamine resin plus 1% amine hydrochloride catalyst, air dried, not washed.
M-12	15% unmethylated melamine resin plus 1% amine hydrochloride catalyst, cured 180°C, not washed.

TABLE VIII

Effects of sunlight exposure on resin treated vat-dyed cottons.

Under Glass

Code no. of dye[1]	Exposure time: 10 hours C[2]	10 hours E[3]	10 hours M[4]	20 hours C	20 hours E	20 hours M	40 hours C	40 hours E	40 hours M
3-L	5	4	5	5/4	4/3	5/4	4	3	4
4-L	5/4	4	5/4	4	4/3	4	4/3	3	4/3
5-L	5/4	5/4	5/4	4	4	5/4	3	3	4
6-L	5	5	5	5/4	5	5	4	5/4	5/4
8-L	5/4	5/4	5/4	4	4	4	4/3	4/3	4/3
11-L	3	3	4/3	3/2	3/2	3	2	2	3/2
12-L	5/4	5/4	5/4	4	4	4	4/3	4/3	4/3
26-L	5	5	5	5/4	5/4	5/4	4	4	4
27-H	5	5	5	5/4	5/4	5/4	4	5	4

Not Covered

Code no. of dye	Exposure time: 10 hours C	10 hours E	10 hours M	20 hours C	20 hours E	20 hours M	40 hours C	40 hours E	40 hours M
3-L	5/4	4	5/4	4	4/3	4	4/3	3/2	4/3
4-L	4	4/3	4	4/3	3	4/3	3	3/2	3
5-L	4	5/4	5/4	4/3	4	5/4	3/2	3	4
6-L	5	5	5	5/4	5	5	4	5/4	5/4
8-L	3	4/3	4/3	3/2	3	3	2	3/2	3/2
11-L	3	3	4/3	2	2	3	2/1	2/1	3/2
12-L	4	4/3	4/3	4/3	3	3	3	3/2	3/2
26-L	5/4	5/4	5/4	5/4	5/4	5/4	4	4	4
27-H	5/4	5/4	5/4	4	5/4	4	5/3	4	4/3

Legend: L = light shade (0.25%); H = heavy shade (2.0%)
C = control, no resin treatment
E = ethylene, urea resin
M = melamine resin

when aftertreated with thermosetting resins, and that the higher the concentration of the resins, the greater the fading to expect. However, from previous experience one cannot rely on the properties of individual dyes in this effect, but must check each combination. Also from the practical standpoint, it has been shown that, in general, washing after curing will reduce the light fading effect where it occurs. It has also been shown that the finisher need not be concerned about choice of catalyst as long as it is one of the types used in these experiments, ie, a chloride catalyst, nor about the curing temperature. If the effect is going to occur, it will occur without curing taking place or without a catalyst being present.

It is planned to check the results obtained thus far and to carry out further experiments with additional dyes and additional catalysts to broaden the scope of the information obtained. It is also planned to determine the mechanism of the reaction by which the $-NCH_2OH$ group increases the light fading of certain vat dyes.

It is further planned to study the effect of the resins on the light fading of combinations of vat dyes, for both theoretical and practical purposes.

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Perkin Centennial International Day———

COLOR—THE CATALYST OF COMMERCE*

PANEL

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Consultant

J ROBERT BONNAR, *moderator*
General Dyestuff Co

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Good Housekeeping Institute

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Textile designer and colorist

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Radio Corp of America

Panelists from other countries:

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The T Eaton Co, Ltd

WERNER KUNZ, *Switzerland*
Heberlein & Co, AG

CLIFFORD PAINE, *United Kingdom*
Imperial Chemical Industries, Ltd

Question: What is the function of color in package design?

Albert Kner (Container Corp of America): Commercial designs consist of a variety of design elements, each of which has a certain assigned function. Because color is the shortest visual path to human emotions, it is one of the most important elements. Color is, first of all, a problem of organization because its effectiveness in arousing emotional and high impact appeals depends upon the manner in which it is integrated into the overall design. Secondly, color is a problem of association—that is, color may suggest different physical characteristics, such as softness, harshness, high quality, low quality, and so forth. Color has subsidiary significance as an element of identification because human brains do not effectively retain color impressions conveyed by colored objects. The principal significance of color lies in its ability to create or eliminate a receptive climate for other design messages to be absorbed.

Question: How can we evaluate the effectiveness of color as a merchandising instrument?

Mr Kner The Design Laboratory has developed various pieces of testing equipment which can be employed to evaluate the effectiveness of designs or design elements as merchandising instruments. These testing apparatus, their relative functions, especially in relation to the problem of measuring color, may be explained.

Question: What would you think from abroad would be the future technical developments in the color-making industry?

Clifford Paine (Imperial Chemical Industries, Ltd): Attempting to forecast future technical progress is usually a rash enterprise. My first instinct is to examine the past, which is perhaps not an inappropriate thing to do during a Perkin Centennial Celebration.

Among the outstanding landmarks of the last 100 years of dyemaking was the discovery of dyestuffs with specific affinity for particular fibers and the recognition of the broad chemical and structural factors which determined such specific affinity.

Dyestuff affinity in this classical sense implies equilibrium between dyebath and fiber and usually involves an appreciable time factor in arriving at such equilibrium. With recent developments in rapid and continuous dyeing processes, it may well be that the chemical criteria of dyestuff design will require reconsideration.

It is true that some of these continuous processes—for example, the use of molten-metal baths—produce conditions which favorably influence the rate of attaining equilibrium when using dyestuffs of the classical type of affinity. Nevertheless, it would seem that the dyestuff maker and the dyestuff chemist will have to make future contributions to this new dyeing technology by designing new types of dyestuff structure with the ability to give high rate of penetration and, particularly, to give a high rate of fixation —for example, by polymerization or rapid chemical interaction with the fiber.

The growing multiplicity of new synthetic fibers and the growing desire to use them in a multiplicity of combinations in order to get the maximum range of textile effects seems to me also to focus attention on this same problem since this surely is a context in which classical affinity is unlikely to provide an answer. I agree, of course, that even in combinations of fibers there will still be occasions when specific fiber affinity will have its merits in order to achieve a special coloration effect.

Question: Is it your opinion that the introduction of solution-dyed man-made fibers will expand the use of the fibers and if so, what end uses?

Harry L Dalton (American Viscose Corporation): First, let me cite a few of the more important advantages of solution-dyed fibers. One advantage is, of course, colorfastness; colorfastness to atmospheric fading, exposure to sunlight and washability.

Possibly even more important is the fact that the color is completely dispersed all through the fibers, and there is never a color fading due to abrasive wear. Consistent uniformity of shade is another important advantage. There are many more.

Now then, I want to talk about a few disadvantages, the first and major one of which is inventory. Because of inventory, your shade range will be somewhat limited. It is necessary for reasons of cost and production facilities to produce these yarns in large quantities.

* Presented during the afternoon of September 10, 1956 at the International Day Sessions during the Perkin Centennial at the Waldorf Astoria, New York, NY.

Another point for consideration is the time factor. Solution-dyed fabrics cannot be prepared for market distribution as quickly as can piece-dyed fabrics. The reason for this is obvious.

In many end uses the advantages by far outweigh the disadvantages. I think that solution-dyed fibers will serve the work clothes, drapery, upholstery and automotive industries best, and while our man-made fibers were not, in the past, extremely important to these end uses, they will now become so. This provides a typical illustration of color becoming the "catalyst of commerce."

Question: How is color influencing the growth and expansion of the man-made fiber industry?

Mr Dalton: That branch of the man-made fiber industry with which I am most familiar, rayon and acetate, owes much of its growth in the apparel and home furnishing fields to color. These fibers have high consumer appeal of themselves, and with the addition of an almost unlimited range of brilliant, appealing coloration, a most attractive fabric with the required degree of fastness is the result.

Color has been an important help in the building and the expansion of our yarn-producing industry, but let me now offer a word of warning that color can, if not properly applied and judiciously selected, be a means of impeding consumer acceptance. It is for this reason that my company has initiated a quality-control program, which, we feel, will provide the incentive for the production of serviceable fabrics containing acetate or rayon.

We are confident that such a plan will provide the consuming public with a three-dimensional fabric, one which offers the advantages of price, fashion appeal and the all-important third dimension of functional stability in which color is of paramount importance. It is this scientific approach which will enable color to further assist our industry to continued expansion.

Question: What influence has color upon the development of the textile industry?

Werner Kunz (Heberlein & Co, AG): The importance of finishing textile goods was recognized very early. This becomes evident, for instance, when we read a decree by the French statesman and economist Colbert (1619-1683) wherein he writes—in a free translation:

"It is true that silk, wool and linen maintain and promote trade, but the soul of it all—without which the body would lead but a very poor life—is the art of dyeing. It imparts to the fabrics a variety of lovely colors, making them desirable and creating thus anew the beauties of nature."

It has been clearly pointed out here that it is color which makes a fabric desirable. The application of colors to textiles for this purpose goes back far to pre-Christian times, in China for instance, as far back as the year 2,000 BC. Also to other civilized peoples, like the Indians and Egyptians, the art of dyeing was already known at a very early stage. It is not exactly known to us how the application of color to textiles was practiced originally, but we may assume that the methods were very similar to those in use nowadays by the primitive races. The primitives in the tropics who wear few or no clothes at all paint their bodies with gaudy colors, to satisfy their inborn "hunger for color." We may well say: In the beginning there was color.

For the Chinese, the color of their clothes was highly important, which is shown by the fact that clothes of a certain color were the privilege of a special class; for instance, only the emperor and empress wore yellow; the imperial ladies violet, the knights of the first grade blue, and so on. This desire to distinguish one's own person from others made man search in olden times for coloring matters. He found them in nature's own dyestuffs of animal, vegetable and mineral origin. The old Chinese knew vegetable indigo and prepared Kermes dyestuff from a scale insect.

The use of color as a symbol for power and wealth can be traced right through to the middle ages. For a long time only persons of superior rank were allowed to wear bright colors; the common people had to dress in dull shades, mostly grey and brown. From this time originates the distinction between the so called "schoenfaebern" and "schlechtfaebern." This had nothing to do with the quality of the dyeing itself; it meant that the "Schoenfaeber" dyed in brilliant light colors for the people of rank and the "Schlechtfaeber" in dull colors for the common people. These social distinctions between the classes, as demonstrated by the color of their clothes, disappeared when the common people gained increased liberties. The craving for color and the desire of the common people to imitate their betters led to an ever-increasing demand for brightly colored fabrics.

Colored textiles played an important part in war at all times. The warriors of the middle ages wore the gay colors of their respective banners, which at the same time served to distinguish friend from foe in the man to man fights. Today tent-cloth and nets are printed with artfully combined colors to camouflage military targets.

Innumerable examples could be cited to show how, in the course of development, textile dyers and printers have been confronted with ever new problems. Until far into the 19th century it was their skill and know-how mostly that helped them to meet the demand for colored textiles. It is astounding to see what experience and skilled workmanship achieved in the domain of fabric dyeing and printing long before the introduction of the synthetic dyestuff.

The development of the new dyes, and especially the amazing progress in the field of the dyestuff industry, have made it possible for the dyers and printers to comply with the most exacting, even craziest wishes for fashionable shades. The spur of the rapidly developing printing and dyeing methods for textiles has always been the desire for color. Whereas the elaboration of these methods pertaining to classical textile materials, such as silk, wool and cotton, required thousands of years, a similar process is being repeated in our days on synthetic fibers in an amazingly short time. The artificial fibers, from the regenerated types to the newest synthetic ones, brought along no end of difficult dyeing problems. Thanks to the efficiency of the dystuff industry, quite a number of these difficulties have been overcome surprisingly rapidly.

We may claim that the introduction of synthetic fibers for clothing on a relatively broad basis would not have been possible had not the problem of dyeing been solved in such a short time. The application of color to these new fibers was certainly a great help in opening the road to the use of this new material in daily life.

As we realize more and more that color has a psychological effect upon the human being, we also realize the importance of color in connection with the atmosphere of the modern home. Thus interior decoration and color combinations for upholstery become brighter. The colorful atmosphere of the interior influences in turn our wearing apparel, and so it is color again that increases the demand for textiles.

Clothes are not merely a protection

for the body. They represent for a large number of human beings primarily the expression of fashion. The ever-changing fashion and the desire for change in colors increase the consumption of textiles. From time immemorial the "hunger for color" has spurred dyers and printers to achieve ever more manifold and subtle colorings on textiles. In hardly any other field does the day's slogan apply more adequately: "Color—Catalyst of Commerce."

Question: As it relates to finished fabrics in the textile world, is color, in fact, a catalyst in commerce, and if so, in what respect?

Jackson E Spears (Burlington Industries, Inc): Without seeming to deprecate the recent importance of color in the automobile industry, I feel that, generally speaking, color plays its most important and most fundamental function as a catalyst of commerce in the textile field.

Clothing is worn for the following reasons:

1) To provide the comfort of warmth.

2) To provide the comfort of modesty—which may in itself be something of a fashion.

3) To provide comfort for the human spirit.

It is in this latter regard that color plays its greatest part.

The textile industry would be a dull business indeed and the human being a dull character if the clothing business were restricted to a single drab color which provided the necessary cover and a reasonable degree of warmth.

The uses of color in textiles are so vast, so far-reaching and so important that I think I can handle it best by listing some of the principal purposes served by the use of color in all its varying forms.

1) Human beings don't want to look like each other.

2) Color is important both as a reflector and an affector of moods and tempers.

3) Color relieves the boredom of the eye.

4) Color can serve utilitarian purposes, such as camouflage—whether in love or in war.

5) Color can enhance the comfort of a garment—through heat reflection or heat absorption.

6) Color properly used can improve contours and make pleasing to the eye what otherwise might not be so—through emphasis and de-emphasis.

7) Color catches the eye, thus through the excitement of curiosity improves sales.

8) Color can be used to stop traffic—and not just with street lights.

9) Color excites travel. People will go to Switzerland to see the edelweiss bloom; to Texas for the blue bonnets. They write sonnets about roses and see beauty in the dark rain forests—and fortunately they need wardrobes for travel.

10) And last, but not least, a new and exciting color soon loses its glamour and becomes relatively unattractive, and out of this comes obsolescence which requires replacement of wardrobes.

Therefore, it is very clear that in the distribution of finished textile products of all kinds, whether for textile apparel usages or for industrial purposes, color is a great catalyst of commerce in developing sales and satisfying consumers. It is our greatest ally.

Those of us particularly interested in quality, or to phrase it another way, those of us interested in the repeat business which we get from satisfied customers, have a very healthy respect for color. And, certainly, we, in the textile business, owe a tremendous debt of gratitude to the great Sir William Perkin for his discovery of synthetic colors and the doors it opened for us to increase our business many-fold.

Question: You have often stated color is one of our most important means of projecting a new idea and of achieving success for any given objective, particularly as related to the textile story in the home furnishings field. Could you develop this idea for us and tell us, now that we have had a mauve era and a red plush era, what is the next era coming along?

Dorothy Liebes (textile designer and colorist): I didn't know I was to be cast as a seer, but seriously, color is the staff of life. While designers give us scale and dimension, we also have this wonderful tool—color—with which to work. I do not need to remind you that color has the greatest impact of the elements of design. For instance, if a lady shopper sees a colored item across the floor, she goes over, looks at it, feels it, and then asks the price in just about that order. So there we have it—this wonderful instrument, color, the most important part of our textile story.

Yesterday, in wandering through the Egyptian section of the Metropolitan Museum, I looked at the wall paintings and the Coptic and Egyptian fabrics—all very beautiful. Yet I was struck by their unbelievable paucity of color.

We have no such restriction today. The sky is our limit, and we have at our finger tips an enormous color pallet. Psychologically we don't know exactly how to measure it, but economically we do. Color cycles are not entirely happen-stance, they are man-made, and there is no point in being naive about it.

For one thing we can forecast a year ahead because we have certain dyes that must move in a certain direction. Correlation is the order of the day, and I might remind you that I don't completely agree with Mr Spears about our not being regimented. I think we are very regimented. As I look around this room —this isn't Madison Avenue to be sure—it is the grey flannel suit era. There have been periods when man wore much more exciting and beautiful colors than they do now. However, I believe we are on the threshold of an era of beautiful and exciting colors for men.

Now, I think the most important thing is not color itself so much as its correlation with other colors. Delacroix said, "Give me mud and I will make it sing." How color is used: the proportionate amounts, the scale (one color weighs too much; another weighs too little) shows the artistic skill with which colors are put together. We could even say composed. We must consult our pallet constantly. We must remember that it isn't enough just to look at colors. We must study the pros, the great painters of the world. Great artists and nature are a source of inspiration that never lets us down. Somewhere, at some stage, you will be inspired by beautiful use of color in a work of art or swept by the beautiful color schemes in nature, as, for example, the Mohawk Trail in autumn foliage.

I am very proud to speak here as a designer and for the designers. I cannot omit our debt to Sir William Perkin and the creative scientists who have worked with him through the years in laboratories to provide us with remarkable dyes. Thanks to their efforts we have the most wonderful magic instrument with which to tell our color story.

Question: Is color important in the Canadian retail field?

J W Eaton (The T Eaton Co Ltd): Mr Chairman, when I looked at the nicely alliterative title for your panel presentations, I felt that I could add another "C" to the existing three to make it "Color—The Catalyst of

Commerce in Canada," for though Canadian merchandising is inevitably strongly affected by the practices of our great neighbor to the South of us, we do have certain ways of our own in utilizing the use of "color" in merchandising.

Is color important in the retail field? The answer is emphatically "yes." Our color consciousness has been sharpened through the large circulation of magazines both from Canada and your country that feature fashion and home furnishings, to say nothing of the advertisements from the motor car industry. We use color for appeal to the shopping public and also to make our stores more pleasant for our employees. There is color in our displays to attract attention where desired, color in our packaging to promote impulse buying, and color in our merchandise for appeal and to tie in with today's ideas of modern living. There is no doubt about it, Canadian people love and respond to the effective use of color in the retail trade.

Question: Color is important in safeguarding life and limb, in factory, home and on the street. For instance, if it weren't for color, our traffic system would become snarled up. In your experience, what are some of the problems you have encountered in the use of safety colors?

Arthur S Johnson (American Mutual Liability Insurance Co): I am afraid that I will have to take you out of the textile field for a minute. Nothing that I have to say deals with the textile field or textile colors, but you must all remember that color has been used to designate dangerous places and safe places ever since there were such things.

Red and green are colors that naturally come to your mind when you think of danger and safety. There are red and green running lights on ships. There are the red and green stop-and-go signals in traffic. Color also has been used in recent years to designate dangerous parts of machinery and, believe it or not, in a cable of thousands of telephone wires each individual wire is designated by a color to make it a separate article from the rest.

Now, this question of color in safety is one to do with people and not with color itself. I refer to color blindness. People who are color blind cannot distinguish green and red. There are a million and a half people driving cars today who have to have some assurance that when they see green it is green and when they see red it is red. The United States Bureau of Standards set up a committee under a man named Keegan to see if it could discover a green that was distinguishable from red and a red that was distinguishable from green. They found that, if the colors were pure enough, that is, green without some red and red without some green, and they were practical of producing in glass coloring, they would serve quite all right.

So, referring to the very highly technical chromaticity diagram of the CIE, it has been possible to spot exactly the green that is useful and the red that is useful. The American Standards 53.1, 1953 is a code which designates hazards and designates safety. You might want to get a copy of this code. It is rather useful with respect to this question of catalyzing commerce with color because paints and plastics and the rest of the things that are used in commerce are sold also for traffic signals, traffic signs, safety signs, etc. The exact chromaticity of these colors is correlated to several color systems, such as the Munsell Color System and others.

Let's say, Mr Chairman, that the problem of color blindness is something to consider. One railroad solved it by getting rid of color and using position signals, but it has been solved also in the red and green traffic lights that you see today which are distinguishable by all drivers.

Question: I understand that color has tremendous impact in the field of advertising. Is this a recent development, or have we been exposed to it for a number of years? Can you tell us something of the origin and development in major advertising areas?

John A Cairns (Anderson & Cairns, Inc): I think that everything that Mr Spears and Mrs Liebes have had to say about the impact of color in textile manufacture and design goes double for the advertising business. From where I sit, I would say that the uses of color in advertising are just about as important as the use of any one of the major advertising media. I think that people have always been conscious of that fact. If you stop and think about it a moment, you will realize that the tones of gray and black have always been considered the symbols of gloom and despair, and these words are hardly the proper psychological background for a successful selling program. So, I think the use of color in various forms of advertising has been here as long as we have had advertising practitioners.

Now, there are two problems involved. When it comes to the forms of advertising where color can be applied by hand, as in direct mail posters and bill boards, etc, we have had color with us for as long as anyone here can remember; but when it comes to the application of color in mass advertising media, we have a different problem, and we have also the situation where the developmental work has been emphasized or accelerated within recent years. There are four dates to remember:

In 1893 there appeared what was considered the first magazine advertisement in full color, which was run on the back of *Youth's Companion* by the Mellons Food Company.

There was then a lapse of ten years before Mordel Brothers Department Store in Chicago ran a full page advertisement in two colors in the *Chicago Tribune*.

There was another long, long lapse in the development of color in advertising until 1927, when the Electric Utility Company of Milwaukee, Wisconsin, ran the first full-page newspaper advertisement in full color in the *Milwaukee Journal*, a paper that has, incidentally, done a perfectly wonderful job in the mechanical developments necessary in bringing about color in newspaper advertising.

Finally, I think, the last big milestone in the history of the use of color in mass advertising media occurred in December, 1953, when the Federal Communications Commission finally approved compatible standards for commercial television. That is the latest big, exciting development in our business as far as the use of color is concerned.

Question: Do we have any means of measuring color's present value to advertisers in terms of their annual investment in color advertising, in terms of the additional value of color advertising, or in terms of sales results?

Mr Cairns: We certainly do. If figures talk, and I think they do, it might be interesting to contemplate the fact that in 1955—as nearly as could be estimated—the total investment that American business firms made in advertising approached the $9 billion mark. That is a lot of money. As far as the box score is concerned, I think the statistics are quite interesting for the portions of the industry where we have any worthwhile statistics.

First of all, trade papers. In the field of trade papers, it is estimated that about 65 percent of all the advertising in 1955 appeared in two or more colors. Consider that this is a fairly

recent development with most of it taking place in the late 1920's. I think that you will admit that is tremendous progress.

In the field of national magazine advertising, it is estimated that about 50 percent of all the advertising in magazines appeared in color in 1955.

When you come to newspapers, leaving out the Sunday supplements and the special sections which are printed separately and apart from the rest of the newspaper, it is estimated that 2 percent of the total appeared in color in 1955. You may not think that 2 percent is a whole lot, but as nearly as we can figure it adds up to 89 million agate lines of advertising and represents an increase of 50 percent in two years.

When it comes to television, Mr Seidel will undoubtedly cover this aspect and do a very able job at it. I can go along with him a hundred percent in his enthusiasm for the value of color in television advertising and in his optimism for the tremendously rapid use of color in this new and exciting field in the next few years.

What about results? I don't suppose there is a business in this country that has more thoroughly and continuously surveyed as the advertising business. Surveys in the use of color in advertising have been going on constantly, being sponsored by major advertising media, by advertising agencies, advertisers and independent research organizations, and as far as I know, no one has ever conducted a survey on the use of color in advertising that did not clearly demonstrate the fact that color attracts more attention, creates more inquiries, and makes more sales per dollar investment than black and white advertising. So I think we can safely assume that color in all forms of advertising is here to stay and will get more important as time goes on.

Question: What are the basic factors in color problems as related to the plastics business?

L Kenneth Merrill (Bakelite Co, Div of Union Carbide and Carbon Corp): I think it is rather obvious that the question is pretty broad and probably will have to be broken down into at least two categories.

It certainly is true that the practically infinite color combinations which are available today in our commercial plastics have been a tremendous boon to their trade acceptance. That is probably more true in the consumer field than it is in the industrial field although, as one of the panelists has mentioned, color in industrial application, such as in the wire and cable industry, is very important. These color problems pose some very real difficulties.

In the first place, we must be continuously alert to the requirements and demands of people who have a highly developed aesthetic sense, which we, in the plastics industry, could not claim to have. This is particularly necessary because we, as material suppliers, must supply to the fabricator the kind of color he wants with the required degree of uniformity and at a time he wants it. Of course his demands will also include those of the ultimate consumer.

This situation poses problems for us which are somewhat different, I think. They have always existed in the textile industry, for example, but they are somewhat complicated by virtue of the fact that our processing conditions on plastic materials are radically different than they are in the textile, paper and other industries.

Another phase of the question, I think, could be touched upon in this way: the matching of colors from lot to lot with the accuracy required in the present economy is sometimes difficult because, in many instances, we are not dealing with the same base color in the material that we started from. Therefore, it is a batch-to-batch proposition, and frequently that batch problem is on a relatively small scale.

Then there are also the very stringent requirements of maximum stability and durability of that color. This is contributed to by the fact that light and weathering factors introduce a chemical change, which in turn may mean a chemical change to both the plastic and the colorant that may be involved. We are, therefore, very often in the position of integrating the effect of those changes on the end result, which is the visual color that you or the consumer accepts.

Another factor that enters into this, which is somewhat different than with our friends in the textile industry, is the fact that, in compounding colors in plastic, one generally deals with processing conditions which call for relatively high temperatures—300 to 350° F and upward. Therefore, these temperature conditions pose possible variants in color, which may be due to the plastic or colorant used. For these reasons the testing and control of color becomes very important.

Question: How is color selected by the automobile companies?

Robert Bingman (Chrysler Corp): In the first place I'd say that the procedure is involved—quite involved, in fact. After all, it calls for working on the emotional side of the design, and that is a little hard to reconcile with our engineers and other people. There is such a close tie between design and color that, of course, our decisions are tempered a great deal by past public acceptance and how much time is involved in developing the design. Sometimes they are a little contrary to those of the previous year when surveys have indicated another direction. So, it sometimes becomes quite a hassle to get everybody together on common ground.

We do have a procedure, and although I can't speak for the whole industry, certainly not authoritatively, I believe our procedure at Chrysler is pretty common. Actually, the question is pretty far reaching, and to answer it from all viewpoints would take considerable time. However, it might be worthwhile to outline the phases we go through in selecting these colors, because we really take it seriously.

There are only a few colors that will occupy the attention of the public at any one time. It boils down to finding out or anticipating, for instance, what those colors are that occupy the public's attention. For automobile use, we can't afford to overlook anyone that uses color. We find the public's color preference in other consumer goods affects their automobile preference also. Thus we have to gather our color information and data from any and every source available.

Then we have to interpret the data and select those colors which we hope will be popular and becoming to the car interiors and exteriors. To do this we have a color-styling studio staffed with various color and paint experts, which acts as a clearing house in all color ideas and then sets these ideas up in the form of presentations for management selection.

Briefly the selection phases are this: Color stylists work up with the major paint experts anywhere from twenty to thirty new colors each year. They then proceed to paint up small plastic models in these new colors, and we simmer this selection down to what we call our styling jury. This is composed of our directors of styling, the chief stylist of our particular car division in question, the head color stylist, the manager of the interior fabrics and other complementary styling people. The purpose of such a jury is merely to weed out those colors that they feel the management would not consider. The accepted colors from a styling

viewpoint are then shown to management and they, in turn, select from these colors their production line-up.

Now, to consider the job of the exterior as compared to the interior. This is a complete story in itself, but I would like to make this one comment. What you can do colorwise with material fabrics has more implications than what you can do with exteriors, and with the importance of keying exteriors to interiors we have on many occasions reversed the procedure. I mean that we have selected interiors first and then matched the exteriors with the interiors.

I would like to cite a few statistics of the things you run into. Each year we are shown something like 5,000 colors by six of the leading paint companies in America. From a corporate standpoint we have to release and master some 600 color items each year. We maintain our own color library, which systematically has, I might add, over 30,000 color chips. That is just the general procedure.

An automobile is a pretty dressy piece of merchandise, and a more aggressive color sometimes complements it. We have in a number of executives from the industry who interest themselves in these things. Sometimes it is a little difficult to get them to temper their own taste with some colors we think might be more fitting in the product.

Question: What is the present status of color television?

Robert A Seidel (Radio Corp of America): As far as the television industry is concerned, this is the year of color. Color television is here. The technique has been fully developed.

All that has been needed to get it kicked off is the decision of the nation's broadcasters to offer top-flight color programming with sufficient frequency to meet consumer demand, and for the set manufacturers to find manufacturing economics that would enable us to put a set out at the price which the mass market can afford. I think both of these things have been done.

Beginning almost immediately the National Broadcasting Company will offer its viewers at least one hour of color programming every night in prime listening time—sometime between eight and ten o'clock. In addition to that, on Saturdays and Sundays, we are likely to have three straight hours of color broadcasting. Further, every afternoon, or practically every afternoon, will feature a drama of one hour in color.

Other networks are augmenting their schedules. A great many independent stations have gotten their own color equipment, are originating programs, and doing a grand job of it. The NBC station in Chicago is now broadcasting entirely in color and soon to follow suit will be Philadelphia, Washington, and all the other stations that are owned by NBC.

We recently studied a survey of Elmo Roper's, which shows that more than a million people have indicated a desire to buy color at the price at which it is now being offered, and at least three of the major companies outside our own have offered sets from the hundred to the five-hundred dollar mark. We believe that the prices are right, the quality of the product is good, the banks have seen fit to come through with very liberal finances or financing plans for color, the networks have stepped up their scheduling, and the service companies have brought prices down. We think that we have a product now that the public can afford to buy and that they will buy.

I would like to touch for a minute on just what color means. In the ten years that we have had black-and-white television, more than 43 million sets have been sold to consumers. That has meant a total retail volume for the sets alone in excess of $13 billion. We expect that, starting now, color is going to follow a similar pattern. Our best guess as to what will happen to color set sales in the next ten years is a volume of 53 million sets at retail prices of more than $16 billion.

Figures of this kind provide a very powerful stimulus to the entire country at every level.

I might add that, in our company alone, we employ 80,000 people and we are only one of the manufacturers of television. There are upwards of thirty in the country. We have 7,500 companies from which we buy goods to help provide the services needed to furnish our consumer products. Not only has television created a new industry and one that is going to rise even to greater heights with the advent of color, but television as an advertising media has become the world's most powerful marketing tool.

I almost had a fit a while ago when Mr Cairns mentioned everything but television at the start of his talk. I wrote him a note and he came through toward the end. Color television has resulted in millions of dollars of sales. Nowadays it is possible to market a program overnight. You don't have to go through the business of lining up two or three hundred stores to advertise it or acquaint with color. We put out spectaculars in one night with listening audiences as high as 55 million. Anything is possible with television. It brings together instantaneously, in sight as well as sound, the most widely separated places, the most interesting events. With the advent of color it is going to be more effective and it certainly is going to provide even more stimulus to the nation, not to mention the value of entertainment, culture, information, education. Thank you, very much.

Question: What has been your experience since adopting American Standards L-22?

John E Reeves (Reeves Brothers, Inc): As most of you know, L-22 is a standard set up by the American Standards Association to define minimum performance for textiles. The net effect of our placing the Bishopville Finishing Division of Reeves Brothers under a control plan based on L-22 has been a substantial savings in cost. This is not to say that putting in a quality control system does not cost money, but we do say that the net result has been an actual reduction in our cost of doing business. It is a fact that we enlarged and modernized our laboratory to handle the burden of checking and testing our production on a continuous basis. Also, we find that we are using better dyestuffs. But, since all this has been accomplished, we have experienced a number of savings in costs which more than offset the costs of this control.

For example, we now have an inventory of dyes and chemicals, all of whose properties have been laboratory registered to assure quality production. Furthermore, every lot of dyes and chemicals shipped to us is checked against these standards. In other words, we have taken the guess work out of what we can obtain from these products in terms of performance dependability, and this has simplified our purchasing operation at the same time. In addition, the most important saving in cost of operation has been the absence of customers' complaints or returns. Every yard of goods we ship processed under L-22 we know will be satisfactory on all counts, without reservation.

We can assure you that a performance standard is not an expense. Rather it is an investment which will yield tangible savings in operating costs.

Where else in our whole economy is an industry of any consequence that operates without specific performance

standards on all component parts, resulting in a guaranteed finished product?

With thousands of suppliers selling to the public their product, chemicals, fibers, fabrics, color, sewing, etc, I think the consumer is thoroughly confused. The consumer is not technically conscious enough to analyze dyestuff, fiber, weave, finish and sewing on the spot to determine the best garment to purchase for its end use serviceability.

Each segment of the textile industry owes itself and the consumer a package—a garment guaranteed to give satisfactory performance. Then, and only then, can we consumers buy with confidence.

Question: How do you think color can be made of greater merchandising significance in the textile field?

Mr Reeves: Obviously, color has always played a vital role in textile fashions, for without color a textile is without appeal. One has only to think of the whole history of fashions to appreciate the role of color in the apparel industry. I doubt that there will ever be a lack of imagination among the textile designers in the employment of color to create new fashions in fabric, but I do feel that color will never attain its maximum acceptance and appreciation by the consumer until higher standards of performance and dependability are assured.

It's strange that in an industry that spends so much money on fabric creation, more interest is not shown in assuring performance dependability of its product. As the life of the product is so closely linked with the lasting qualities of color, it seems to me that, before we can realize our greatest opportunities as an industry, we will need to make greater use of performance standards.

Question: What effect has the introduction of color in appliances had on the appliance industry? What is the general consumer reaction to color appliances?

Willie Mae Rogers (*Good Housekeeping Institute*): Could I say something else before I start into that? I feel so pleased because at long last Mr Reeves remembered that there is such a thing as a consumer.

I have been sitting here listening to all the questions and answers and thinking, as I do many times in similar discussions, that sometimes those of you who develop not only color but the products for the consumer maybe do not stay as close to that consumer as you well might. There is nothing truer, I'm sure, than Mr Reeves' comment that the consumer is many times confused about color. I would like for you to come up sometime and let me turn you loose with our reader mail. You would find all the proof you would want.

It is true, in every phase of anything that the consumer buys for her house and her family today, that problem enters into it very vitally. The appliances are just one phase of it. I think maybe Mr Seidel may want to shush me up about what I am going to say about color in the appliances because he is interested in that too, but I am a rebel, not only by birth but by nature, so he will have to take his chances along with the rest of us.

I think color in appliances probably is a thing of mixed emotions to everybody. Certainly it has proved to be a wonderful sales tool. It has brought more people into retail stores, and that is one of the great objectives of all merchandising today. Once a woman gets there she is very likely to look at color but usually sticks with the tried and true white. Actually the major manufacturers tell us that their color sales in appliances amount to 10 to 20 percent of their total volume.

Not too long ago, when I was getting up some information for a talk to the refrigerator engineers, I did a little survey of my own. I made a sort of direct woman-to-me survey, and the women had this to say about color in appliances:

They are a little bit afraid to trust a color to be stable enough. That is to say, if they buy a refrigerator today they may have to wait three or four years to buy a range or a piece of laundry equipment, and if they are going in for color, they certainly want to match the pinks or the aquas or whatever color they choose; but they are afraid they won't be able to do it, and in looking at some of the many lines we see today I think their fears are justified.

I think manufacturers will admit that same thing. Some women are a little bit leery about buying a major piece of equipment in color, although they love it. There is no question about what it does to their spirits in the kitchen, and carrying it further, in their whole house, but when you put several hundred dollars into a piece of equipment that you know you are going to have to use ten, twelve, fifteen years, you have to take many things into consideration. For some strange reason women have never been able to convince the men who write the checks that appliances should be traded in as often as automobiles! It just doesn't seem to work that way.

I know also that color presents a headache to distributors and dealers in that it is an inventory problem. You can see that color in appliances is a mixed-up thing. Nobody knows how it is going to be stabilized. I expect it is here in some form for always. I hope that is true, but it is going to take a little while to get it stabilized.

I have had any number of women say to me, "Why don't manufacturers standardize the colors as they have done in automobiles?" I think they have done it in automobiles. Isn't that right, Mr Bingman? Maybe that is a step forward for the appliance industry to take in the future.

Straight color has proved a great morale booster to the appliance industry at a time when they could stand it.

Question: In a tremendous growth of the use of color in all fields there have arisen, of necessity, many problems. What do you consider the major problems facing manufacturers regarding the use of color in apparel and home furnishings?

Miss Rogers: Again I go back to contact with consumers because I think that is what you all are interested in. Obviously their main concern is that the color be a fast color. I wonder if you have any idea how many times a garment or an item is made with a combination of colors and materials, and maybe the main body of the item is color fast, but some trim that is used is not, and that creates a great dissatisfaction and unhappiness for the consumer. You may think it is unreasonable but a woman sort of feels that if a thing is supposed to be color fast it means all of it and not two-thirds of it or one-half of it. I think that is one of the great problems that exists.

Another problem that confronts all the manufacturers is the problem created by some who want to jump on the band wagon of color without giving enough time and thought to the end use itself. Many times we have products that incorporate the use of color which are completely unreasonable and far-fetched. I won't stop to give you examples but certainly we can show you some if you want to come up to the Institute.

Another thing that has to be faced is that the color or colors in an item should be fast until the end of the life of the garment. It is not enough just to have it fast for one or two wearings

or washings or cleanings. It ought to be color fast as long as the garment, or item itself, is usable.

They are the main things that I have come in contact with in my dealings with women.

We have to bear in mind that we want the merchandise to stand out and not the decoration. The merchandise should constantly be the most important thing you see if you go into a retail establishment. We have found the use of color so pleasing in our surroundings in our industry that one now rarely sees the tried and true serviceable and durable drab colors of the past in any modern store today. As a matter of fact, I doubt very much if you would find many warehouses that are not attractively painted, recognizing that the use of color is more pleasing to the people who work there.

Question: What has the relationship of color been to the chemical industry?

Kenneth H Klipstein (American Cyanamid Co): My main responsibility has been to supply colors and pigments to the consuming industries to do a specific job to help those industries to catalyze their own commerce.

There has been another aspect of dye manufacture which is termed over and above the line of duty. It has had an indirect effect and one which has grown to tremendous importance. The dyestuff manufacturers have been faced with problems of advancing basic science and technology. It was interesting to me, Mr Chairman, to listen to Sir Robert Robinson make his comments about Sir William Perkin . . . that he was not only a chemist but a chemical engineer as well. He must have done quite a job of designing the reaction kettle you saw when he showed the slides. It was entirely new and from that new art it became finally a technology.

Of course it stimulated basic science and technology, and there grew up a vast number of new products, new intermediates which were required for the manufacturer of dyes. These are the products which have led to other industries actually—the intermediates required for dyestuff manufacture.

I would like to point out that aniline, which was the basis of mauve, was not commercialized at the time it was needed. It became commercialized later when it became available at a lower cost. The original cost of mauve was estimated to be about $100 a pound. Since then aniline has been reduced in cost and made available in tremendous quantities, and with its availability there has come such things as rubber antioxigents, without which the rubber industry could not have done what it has.

Another example is the universal photographic developer. That comes from a derivative of aniline. Without that we might not have the photographic or motion picture industry.

Another example is a simple intermediate to make indigo in the first place, but now a basis of the resins. Vinyls have been available commercially for only 20 years, but they are of tremendous importance today.

I would like to mention one or two other examples. Phenol is the old carbolic acid, originally a dyestuff intermediate, and yet it is one of the foundations of the plastics industry. Phenol formaldehyde resins together with celluloid really gave impetus to our tremendous plastics industry today. These are by-products, if you want to call them that, but by-products of tremendous importance.

The interdependence of one chemical upon another and the by-products as the result of that interdependence have given rise to a tremendous impetus in our national economy. The dye industry and the manufacturers of intermediates have made available the dyes themselves, but they have also made available the starting of the raw materials towards a vast number of other industries and applications.

Question: Aside from the use of color in merchandise, are there other ways in which retailers find themselves benefitted in color harmony?

Philip M Talbott (Woodward & Lothrop): Mr Chairman, very importantly so. The influence of color distribution is well recognized by retailers and I am confident retailers are giving attention to its development. Modern retail establishments used color as soon as possible to attract customers. I am sure that color in the use of background for furnishings particularly is very impressive with the great use of color in walls, draperies and floor coverings, and to the costumes the people wear. These colors are designed to hold the interest of customers, to make the surroundings pleasing and to provide a pleasing background to the sale of merchandise.

AATCC Calendar

COUNCIL
Nov 16, Jan 18 (New York); Mar 29 (Roanoke, Va); June 7 (New York)

NATIONAL CONVENTIONS
Nov 14-16, 1957 (Hotel Statler, Boston); 1958 (Hotel Conrad Hilton, Chicago); 1959 (Sheraton Park and Shoreham Hotels, Washington, D C); 1960 (Philadelphia, Pa); 1961 (Buffalo, NY)

MID-WEST SECTION
February 16 (Hotel Bismarck, Chicago, Ill)

NEW YORK SECTION
Nov 16 (Kohler's Swiss Chalet, Rochelle Park, NJ); Jan 23, Mar 1 (Hotel Delmonico, New York, NY); Apr 26, May 24—ladies nite (Kohler's Swiss Chalet, Rochell Park, NJ); June (Annual Outing)

NIAGARA FRONTIER SECTION
Nov 17 (joint ladies night with CATCC at Hamilton, Ont); Dec 7, Jan 11, Mar 15 (Buffalo, NY); Apr 5 (joint meeting with CATCC at Kitchener, Ont)

NORTHERN NEW ENGLAND SECTION
Dec 1 (Annual Meeting—Hotel Vendome, Boston)

PHILADELPHIA SECTION
Dec 7 (Kugler's Restaurant, Philadelphia, Pa)

RHODE ISLAND SECTION
Dec 6 (Annual Meeting, Johnson's Hummocks Grille, Providence, RI)

SOUTH CENTRAL SECTION
Dec 1 (Hotel Patten, Chattanooga, Tenn)

SOUTHEASTERN SECTION
Dec 8 (Atlanta, Ga)

WESTERN NEW ENGLAND SECTION
Nov 16 (Rapp's Restaurant, Shelton, Conn)

Membership Applications

October 19, 1956

SENIOR

Joe T Adams—Research chemist, Carbide & Carbon Chem Co, South Charleston, W Va. Sponsors: K S Campbell, G M Randolph

Arthur S Ashley—Chemist, charge of bleach house, Lancashire Text Processing Corp, New Bedford, Mass. Sponsors: E W Counsell, H Petelle

Mary L Clement—Textile chemist, Everlastik, Inc, Chelsea, Mass. Sponsors, O Hansen, L F Gendron

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Albert L Lefler—Salesman, Emery Industries, Inc, Cincinnati, O. Sponsors: W A Colby, Jr, V B Holland

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Clarence E Pickard—Textile chemical salesman, Onyx Oil & Chemical Co, Jersey City, N J. Sponsors: P D Jacobs, W C Walter, Jr

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Richard C Richardson—Tech supt, Kerr Bleaching & Finishing Wks, Inc, Concord, N C. Sponsors: E R Roper, J C Boesch

Fritz O Robitschek — President, Onyx Oil & Chemical Co, Jersey City, N J. Sponsors: L P Brick, E J Valko

Richard C Scrimgeour—Head dyer & chemist, Synthetic Textiles Mfrs, Rizal, Philippines. Sponsors: J V Moore, O M Lea

Leon Segal—Research chemist, Cotton Fiber Section, Southern Regional Research Lab, New Orleans, La. Sponsors: R K Worner, M L Rollins

Geoffrey Vero—Tech repr, L B Holliday & Co of Canada, Ltd, Montreal, Canada. Sponsors: J Wallace, K A Lister

Anthony R Wagner—Techn, Nat Aniline Div, Allied Chem & Dye Corp, Buffalo, N Y. Sponsors: S J Puliafico, W H Leyking

Bengt Walden—Dye techn, Malmo Yllefabriks AB, Furulund, Sweden. Sponsor: B Ubbesen

John E Warner — Mgr, Coatings Dept, Goodyear Tire & Rubber Co, Chem Div, Akron, O. Sponsors: G H Campbell, W P Welch

Rosser L Wayland—Group leader in Res Dept, Dan River Mills, Inc, Danville, Va. Sponsors: H Y Jennings, H M Chase

JUNIOR

Joseph M Kuschwara—Lab techn & colorist, United Piece Dye Works, Lodi, N J. Sponsors: R Eck, R J DeWitt

Jerrold S Walker — Chemist-colorist, National Aniline Div, Allied Chemical & Dye Corp, New York, N Y. Sponsors: G Altenbaumer, J E Loughlin

ASSOCIATE

Francis E Beaudry, Jr—Chemist & supt of sewage disposal plants, City of High Point, Utilities Dept, High Point, N C

Joe C McDowell—Salesman, Chemicals Div, F H Ross & Co, Greensboro, N C

Benjamin F Purdy—Salesman, Harry Miller Corp, Philadelphia, Pa

William L Schlags — Plant mgr, Acme Summit Mills, Inc, Closter, N J

Zen Z Shorter — Dyer's assistant, Nat Aniline Div, Allied Chem & Dye Corp, Buffalo, N Y

Lathrope Voorspuy — In charge of Physical Testing Lab, Maidenform Brassiere Co, Bayonne, N J

CORPORATE

Emkay Chemical Co
L W Frohlich & Co, Inc
E F Houghton & Co

APPLICATION FOR TRANSFER TO SENIOR MEMBERSHIP

Finis C Whitfield

STUDENT

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Charles D Livengood—North Carolina State College. Sponsor: H A Rutherford

William A Mills—North Carolina State College. Sponsor: H A Rutherford

Roger L Pruitt — North Carolina State College. Sponsor: H A Rutherford

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Helen J Patterson—Georgia Institute of Technology. Sponsor: J L Taylor

Rayford C Ruark, Jr—Georgia Institute of Technology. Sponsor: W Postman

Jules A Bedard—St Hyacinthe Textile School—Canada. Sponsor: G R Boule

Activities of the Local Sections

Hudson-Mohawk

APPROXIMATELY 50 members attended the October 5th meeting of the Hudson-Mohawk Section at the Crossroads Inn, Latham, NY.

The meeting was followed by a guided tour of the Allegheny-Ludlum Steel Corporation at Watervliet, NY.

Midwest

THE 24th Annual Outing of the Midwest Section was held at Browns Lake Resort, Burlington, Wis, June 15-16, 1956. In spite of a rainy week end, 134 members and guests attended the affair. Thirty six participated in Friday's two-ball foursomes. Eighty two started, but only sixty four completed a rainy afternoon of golf on Saturday. Others tried their luck at horseshoes.

Prizes were awarded following a cocktail party and banquet.

The winners of the various golf events were as follows:

Low gross (millmen): R C Anderson—77

Low gross (salesmen): F Kraft—75

Low gross (guests): E T Gurry—77

Twilight golf: 1st—H T Latham and F Connolly, 39; 2nd—J Kelley and R L Burnett, 40

Low net (Flight A): 1st—Art Patton, 89-16-73; 2nd—Art Hultberg, 84-10-74; 3rd—Geo Willgeroth, 79-4-75

Low net (Flight B): 1st—D Anderson, 91-14-77; 2nd—H Anaszewicz, 96-16-80; 3rd—R Lakey, 96-16-80

Low net (Flight C): 1st—A Coleman, 102-22-80; 2nd—B Fay, 103-22-81; 3rd—F Gurry, 101-18-83

Low net (Flight D): 1st—J Miller, 111-26-85; 2nd—J C Baric, 112-26-86; 3rd—W Sites, 112-24-88.

B Isenogle took top honors in the horseshoe pitching — singles event, while the team of V Lawrence and E Cir won the doubles event.

Philadelphia

THE Philadelphia Section attracted more than 250 members to its two-day meeting in Reading, Pa, September 28-29, at which Thomas H Hart, Hart Products Corp, presided.

Tours of the Althouse Chemical Co and Carpenter Steel Co plants preceded the Friday night meeting at the Abraham Lincoln Hotel. A tour of the Sunshine Brewing Co plant and a picnic at the home of C Scott Althouse, president of Althouse Chemical Co, were held on Saturday.

At the Friday evening session, Warren B Reese, Macbeth Daylighting Corp, spoke on "Lighting Factors to Be Considered in Textile Color Matching". Rev Clarence R Rahn also spoke briefly at the session.

Among those seated at the head table during dinner were: Arthur C Melich, Sunshine Brewing Co; F Joseph McDermott, Carpenter Steel Co; Malcolm J Reider, Pagoda Industries; F R Thus, Reading Dyeing Co; Ray Cunningham, president, Reading Manufacturers Association; John Auman, Don Alden, and C Scott Althouse, Althouse Chemical Co; Rev Rahn; Daniel McDevitt, mayor of Reading; Harold De Turk, Berkshire Knitting Mills; William Howard, president Reading Chamber of Commerce; William Knerr, Liberty Dye Works; William Cassidy, secretary, Reading Manufacturers Association; and Alfred Koch, Sandoz Chemical Works.

During the business meeting, the following slate of officers was presented by Arthur Etchells, Hellwig Dyeing Corp, representing the Nominating Committee: *Chairman*—Donald W Robinson, Para-Chem, Inc; *Vice chairman*—William S Sollenberger, American Viscose Corp; *Treasurer*—Albert Stutzke, Globe Dye Works Co; *Secretary*—Ernst Empting, General Dyestuff Co; *Councilors*—Clarence Seibert, Scholler Brothers; Richard Shimp, E I du Pont de Nemours & Co, Inc; Jackson A Woodruff, American Viscose Corp; Carleton T Anderson, Ciba Co, Inc; and Arthur Etchells, Hellwig Dyeing Corp.

The following were placed in nomination as sectional committeemen: Richard C Kopp, Aberfoyle Mfg Co; Matthew Noonan, Becco Sales Co; Isaac P Davis, American Viscose Corp; and John Rogenmusser, Jefferies Processors, Inc.

Rhode Island

THE Rhode Island Section met at Johnson's Hummocks Grill, Providence, R I, on October 18, 1956 with approximately 140 members and guests in attendance.

C Eric Neale, The Apponaug Co, Apponaug, RI, chairman of the Rhode Island Intersectional Contest Committee for 1956, presented the Section's paper, "Roller Printing on Wool", which was awarded third place in the '56 Contest held during the Perkin Centennial. He had on display several dresses and swatches representative of the work covered by the paper.

V Lindsay Chase, director of research and development, Dispersions Dept, Interchemical Corp, presented a 16-mm sound color film entitled "This is Color", after which he commented briefly on the relationship of the science of color to textiles.

In attendance at the meeting was AATCC president Raymond W Jacoby, who congratulated the Section's Intersectional Contest Committee for its work.

The next meeting of the Rhode Island Section will be its annual meeting, to be held December 6th at Johnson's Grill.

Western New England

THE October 5th meeting of the Western New England Section, held at the Hotel Bond, Hartford, Conn, attracted approximately 55 members and guests.

Speaker of the evening was Raymond Thornton, technical service manager, Arnold, Hoffman & Co, Inc, who spoke on the subject, "From Perkin to Procions". This was followed by a technicolor film presentation on color.

The following officers were elected to serve for 1957: *Chairman*—Thomas J Gillick, Jr, American Felt Co; *Vice chairman*—John J Cervini, Cheney Bros; *Secretary*—Andrew W Goodwin, Princeton Knitting Mills, Inc; *Treasurer*—Peter P DuBiel, Cheney Bros; *Councilors*—Raymond J Carey, General Aniline & Film Corp; J Edward Lynn, consultant.

Named to the sectional committee were: Albert H Rant, Laurel Soap Mfg Co; Ernest Otto, Lee Hat Co; Paul W Reeves, Princeton Knitting Mills, Inc; and George C Perkins, Southern Dyestuff Corp.

• PATENT DIGEST •

PAUL WENGRAF

COMBINED EMBOSSED AND CHINTZ EFFECTS———Aminoplasts Applied and Cured G,4

USPat 2,743,190 (Joseph Bancroft & Sons Co——Vonaesch——April 24, 1956)

The preamble to this patent states that processes employing artificial resins for producing goffering (ie, gauffrage or embossed) effects as well as glazed (chintz) effects on fabrics are generally known. *Combination of both effects* was hitherto not possible because an ordinary embossed fabric loses the relief effect upon subsequent glazing.

According to the present patent, this problem has been solved by first printing the fabric with a resin condensate (for instance, a condensate of formaldehyde with urea, thiourea, ethylene urea, dicyanodiamide or phenolderivatives) and then goffering it all over by passing it through an embossing calender. A durable relief effect results after curing. The fabric is then washed to remove the goffered but nonfixed portions, after which it is again impregnated with a similar precondensate by padding, predried at low temperatures, glazed in a frictioning calender, and cured again. It can not be expected that the embossing effect might withstand the following glazing operation.

Example: A tragacanth-thickened melamine-formaldehyde precondensate containing some ammonium thiocyanate as a catalyst is printed on a white or colored fabric and dried at 60° C. After the fabric is goffered in an embossing calender at 200° C, the precondensate is cured for 4 min at 140° C. The fabric is washed and dried, leaving a permanently embossed pattern on a smooth background. It is thereupon impregnated with a melamine-formaldehyde precondensate, dried at 60° C, and passed through a friction calender. The chintz effect is cured under the same conditions as reported for the first step.

Other examples refer to different resin precondensates, to padding all over with the precondensate in the first step and printing a resist to prevent local resin fixation before embossing, to a combined process with naphthol dyes preprinted fabrics, etc.

References cited by the Patent Office:

USPat 2,103,587 (Cal Printer's Assoc—1937): padding with the components of an amino resin, printing a resist that inhibits resin formation (eg, piperidine or glycin, etc), curing and washing out the nonreacted components.

USPat 2,119,150 (Bradford Dyers' Assoc—1938): impregnating of fabrics with an acid formaldehyde solution, treating the fabrics mechanically to obtain a relief pattern, and curing at 110° C.

USPat 2,123,153 (Celanese Corp of Am—1938): printing a fabric with basic, acid or direct dyes plus amino resin components, calendering between metal and paper rollers to obtain a "Ciré" effect (the rollers running at different speeds), curing, and removing the color from the nonprinted areas by washing.

USPat 2,148,316 (Joseph Bancroft & Sons Co—1939): obtaining durable chintz effects by applying a urea-formaldehyde solution, drying at temperature below the curing point and glazing, thus combining finishing and curing of the resin.

USPat 2,454,391 (Cranston Print Works—1948): printing with a methylol-melamine precondensate, drying, glazing, curing and washing. The glazed effect is retained only on the printed areas while the ground appears nonglazed and pliable after washing.

USPat 2,461,603 (Celanese Corp of AM—1949): leading a cellulose acetate (or other synthetic) fabric through a dyebath containing a swelling agent, then between a plain and an engraved roller at room temperature, and finally washing out the excess swelling agent. Delustered areas on bright ground result [cf *Am Dyestuff Reptr* 38, 476 (1949)].

USPat 2,577,957 (Aspinook Corp—1951): running a thermoplastic, eg, nylon or other synthetic fabric, through a dilute amino-formaldehyde precondensate solution, drying to a moisture content of 5-15%, embossing and curing. Increased fusing point of the thermoplastic material has been observed [cf *Am Dyestuff Reptr* 41, 305 (1952)].

PRINTING COMPOSITION FOR THIOINDIGOID VAT DYES ———Metalized Azo-Pigments Added C,5

USPat 2,708,150 (Am Cyanamid——Kienle, Amick——May 10, 1955)

The difficulty in obtaining strong prints of thioindigoid vat dyes of uniform color and good yield has posed a serious problem for many years. This invention aims to provide a stable, nondrying-out color paste which behaves well in high temperature vat agers.

The inventors observed that the desired effect could be attained by incorporating in the printing paste suspensions of azoic dyes, metalized with a ferrous salt as assistant. The pigments are incorporated in an amount not less than 50% of the vat dye, and preferably in quantities approximately equal to those of the azoic dye assistant and the vat dye.

Example: Pigment Scarlet (*CI* 216) was dissolved in water, which was being heated slowly. Hydrated sodium acetate and then some ferrous sulfate were added and the mixture was stirred and heated to the boiling point. The salted-out metalized pigment, washed free of unreacted iron salt and dried, formed the assistant. A press-cake of bis 2-1-naphthioindigo was dispersed with disulfo-dinaphthylmethane. A printing paste was prepared by adding potash and Rongalite to the thickened dyestuff. The metalized printing assistant, as described above, was incorporated in this paste at a ratio of 1.6 p dye solids to 1.5 p assistant. The prints proved to be about 20% stronger than those in which the assistant had been omitted.

References cited by the Patent Office:

USPat 1,945,484 (Gen Aniline/1934): vat dye preparations containing salts of iron, copper, zinc and tin.

USPat 2,327,405 (Imp Chem Ind/1943): dyestuff compositions containing, in addition to a vat dye, not more than 1% of an iron phthalocyanine, calculated from the vat dyestuff's weight.

USPat 2,371,103 (Am Cyanamid/1945): mixed diamides of dicarboxylic acids containing one quinonyl group as printing assistants.

WATER REPELLENT COMPOSITION Comprising Waxes, Isocyanate Derivatives, Metal Salts G,2,02

USPat 2,708,642 (Farbenfabr Bayer——Doser——May 17, 1955)

The hydrophobing compositions protected by the current patent contain three main components:

A) Waxes or paraffins.

B) Higher aliphatic chains containing compounds *capable of forming urea derivatives*, especially isocyanates or polyisocyanates.

C) Polyvalent metal salts, particularly aluminum or zirconium salts.

High molecular isocyanates, eg, stearyl isocyanate, are preferably used in the form of their addition products to bisulfite or formaldehyde bisulfite, also in the form of their amine derivatives reacted with formaldehyde and bisulfite.

Polyvalent metal salts which interact with the compounds mentioned in A or B are generally those that in the prior art have been applied in hydrophobing formulations. Among the various possible Al or Zr salts, compounds not tending to form insoluble hydrolysates upon being heated to 50-60° C are preferred.

In this method the fabrics are first soaked in an emulsion containing A and B, then dried and treated with the metal salt solution, and finally dried and baked. The intermediary drying step in this event may be effected at lower temperatures. Heating at elevated temperatures after applying A plus B is required, however, whenever the metal salt treatment (C) is omitted as described in a copending application (corresponding to German Pat 818.189). Thus the component B is essential in this process.

Example: A weakly acid solution containing the addition product of sodium bisulfite to stearyl isocyanate and formaldehyde is stirred into an emulsion of paraffin, Ceresin and montanic ester. The emulsifying agent is a mixture of sodium oleate and Igepon A. A cotton poplin of the kind used for manufacturing rain coats is soaked therein, squeezed to a pick-up of 65%, and dried at 120° C for 5 minutes.

The dried material is first rewetted by dipping it into a sodium carbonate solution of a Nekal-type agent, rinsed, squeezed and aftertreated with a 0.5% zirconium acetate solution, squeezed again and dried at 100° C. The effect is claimed to be resistant to repeated treatments with gasoline (or, as in other examples, to organic solvents in general).

Amine-type isocyanate derivatives are applied according to other examples (8-10). Here reagents of group B comprise stearyl dipropylene triamine and the addition product of bisulfite to hexamethylene diisocyanate. Otherwise the hydrophobing procedure is analogous to that described in other examples.

Among the references cited by the Patent Office:

USPat 2,314,968 (Gen Aniline & Film/1943): impregnating textiles with monomeric condensates of alkylene imine with higher amino acids, and polymerizing to obtain water repellent effects. (Remark: this patent as well as USPat 2,341,413 apparently cover the "Persistol" process, discussed in *Am Dyestuff Reptr* of March 11, 1946, p 124).

USPat 2,333,917 (Du Pont/1943): coating textile fabrics with one layer of a nylon-type composition and applying on top of this coating a polymeric condensate of an organic isocyanate with linear ester amides.

USPat 2,343,920 (Du Pont/1944): hydrophobing by impregnation with higher amines, drying, treating with higher fatty anhydrides and baking.

USPat 2,430,479 (Du Pont/1947): bonding various materials, such as rubber, nitrocellulose, partly hydrolyzed vinyl acetate, etc, to textiles by adding a diisocyanate, eg, hexamethylene diisocyanate, or optionally, waxes.

WATER REPELLENT SILICONATES Blended with Surface-Active Agents G,2,02

USPat 2,711,967 (Tomarkin——June 28, 1955)

This method is concerned principally with rendering porous surfaces, such as masonry, water repellent, but it may also be of some interest for the treatment of other water-absorbent material.

The inventor advocates the use of water-soluble siliconates, eg, monomeric sodium methyl siliconate, presumed to have the formula

$$[CH_3Si(OH)_2O^-]Na^+,$$

and to lose water upon polymerization in drying. The dried layer does not permit further penetration of another subsequently applied siliconate solution. Deep penetration might impair the hydrophobing effect.

It has been observed that addition of small amounts of selected wetting agents to the siliconates improves the penetrability so that the impregnating process can be repeated.

Example (for the hydrophobing solution): A 20% sodium methyl siliconate solution is blended with a 25% sodium tetradecyl sulfate solution in the proportion 6:0.1. 6.1 parts of this mixture are dissolved in 93.9 parts distilled or demineralized water.

References cited by the Patent Office:

USPat 2,114,042 (Am Hyalsol/1938) refers to the sulfating of higher alcohols after separation from lower alcohols.

US Pat 2,441,422 (Gen Electric/1948): preparing silica sols and silica aerogels, which are useful as stiffening or hydrophobing agents, from silicic acid salts (water glass) and alcohol derivatives of siliconic acid.

USPat 2,574,168 (Wurdack & Brick/1951): rendering masonry water repellent by a treatment with organosilicones.

USPat 2,507,200 (Gen Electric/1950): obtaining water-soluble siliconates by disolving polysiloxanes in alkalis, the compositions to be used as water repellents.

General Calendar

AMERICAN ASSOCIATION FOR TEXTILE TECHNOLOGY, INC
Nov 7, Dec 5 (Both meetings at the Vanderbilt Hotel, New York, N Y).

AMERICAN CHEMICAL SOCIETY (CLEVELAND AND CHICAGO SECTIONS)
Nov 27-30 (9th National Chemical Exposition, Cleveland Public Auditorium Cleveland, Ohio).

AMERICAN OIL CHEMISTS SOCIETY
Spring, 1957 (Spring meeting, New Orleans); Sept 30-Oct 2, 1957 (Fall meeting, Cincinnati); Apr 21-23, 1958 (Memphis); Oct 20-22, 1958 (Chicago); Spring, 1959 (New Orleans); Fall, 1959 (Los Angeles).

AMERICAN SOCIETY FOR QUALITY CONTROL
Feb. 25-27—7th Annual Conference of the Textile Division, Georgia Tech, Atlanta, Ga.

THE DRYSALTERS CLUB OF NEW ENGLAND
Jan 21 (Hotel Somerset, Boston); Apr 26 (Hotel Vendome, Boston); June 21 (Annual Outing—Wachusett Country Club, West Boylston, Mass).

THE FIBER SOCIETY
Spring Meeting—May 1-2, 1957, The Clemson House, Clemson S C

NATIONAL COTTON COUNCIL OF AMERICA
Feb 28-Mar 1 (Cotton Research Clinic, General Oglethorpe Hotel, Savannah, Ga).

PHI PSI FRATERNITY
April 25-27—Annual meeting, New Bedford Hotel, New Bedford, Mass.

THE QUARTERMASTER ASSOCIATION
Annual Convention — Oct 27-28, Conrad Hilton Hotel, Chicago, Ill.

SYNTHETIC ORGANIC CHEMICAL MANUFACTURERS ASSOCIATION OF THE UNITED STATES
Oct 9, Nov 7 (Palm Terrace Suite, Hotel Roosevelt, New York, N Y).

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